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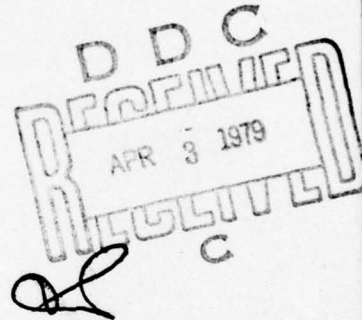
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UNIVERSITY OF TORONTO

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SURVEY OF FLOWS WITH NUCLEATION AND CONDENSATION

by

S. Kotake and I. I. Glass



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## Summary

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## Notation

|              |   |
|--------------|---|
| $A$          | cross-sectional area of flow passage                                  |
| $A_i$        | cluster of size $i$ , $i$ -mer ( $A_1$ : monomer, $A_2$ : dimer, ...) |
| $a_s$        | liquid-solid surface area of heterogeneous cluster                    |
| $a_v$        | liquid-vapour surface area of heterogeneous cluster                   |
| $C_i$        | mass concentration of $i$ -mer  |
| $c_i$        | condensation rate of monomer on $(i-1)$ -mer                          |
| $c_p$        | specific heat at constant pressure                                    |
| $D$          | binary diffusion coefficient  |
| $d$          | nozzle or orifice diameter of free jet                                |
| $e_i$        | evaporation rate of monomer from $i$ -mer                             |
| $G_i$        | Gibbs free energy of $i$ -mer   |
| $\Delta G_i$ | free energy of $i$ -mer formation                                     |
| $\Delta G_d$ | desorption free energy of adsorbed monomer                            |
| $\Delta G_s$ | free energy for surface diffusion of monomer                          |
| $g$          | condensate mass fraction  |
| $h$          | enthalpy per unit mass  |
| $I_i$        | formation rate of $i$ -mer per unit volume                            |
| $i$          | number of molecules in cluster, cluster size                          |
| $Kn$         | Knudsen number  |
| $k$          | Boltzmann constant  |
| $k_f$        | forward reaction rate   |
| $k_r$        | backward reaction rate  |
| $L$          | latent heat of vaporization   |
| $l$          | characteristic length   |
| $l_m$        | mean free path  |
| $M$          | condensate mass   |



|             |   |
|-------------|---|
| $m$         | molecular mass  |
| $\dot{m}$   | condensation rate of vapour mass                            |
| $N(R)$      | distribution function of heterogeneous nuclei               |
| $n_i$       | number density of i-mer                                     |
| $n$         | number density of clusters                                  |
| $p$         | pressure  |
| $p_v$       | vapour pressure   |
| $p_s$       | saturation pressure   |
| $R$         | gas constant per unit mass; radius of heterogeneous nucleus |
| $R$         | universal gas constant                                      |
| $r$         | radius of cluster or droplet                                |
| $S$         | collision cross-section; surface area                       |
| $S_o$       | surface area of heterogeneous nucleus                       |
| $S_s$       | surface area of heterogeneous nucleus wetted by droplets    |
| $s$         | supersaturation, $p_v/p_s$                                  |
| $T$         | temperature   |
| $t$         | time  |
| $u$         | flow velocity   |
| $u_m$       | mean molecular speed  |
| $v_{ml}$    | molecular volume of liquid                                  |
| $w$         | mass flow rate  |
| $Z$         | partition function  |
| $Z_c$       | Zeldovich factor  |
| $\alpha_c$  | sticking or condensation coefficient                        |
| $\alpha'_c$ | effective condensation coefficient, Eq. (48)                |
| $\alpha_t$  | thermal accommodation coefficient                           |
| $\Gamma$    | correction factor for classical nucleation rate, Eq. (72)   |

|           |   |
|-----------|---|
| $\gamma$  | specific heat ratio                               |
| $\delta$  | collision diameter                                |
| $\eta$    | dynamic viscosity                                 |
| $\theta$  | embryo-to-substrate contact angle, Eq. (35)       |
| $\lambda$ | heat conductivity                                 |
| $\mu$     | chemical potential per molecule; molecular weight |
| $\rho$    | density   |
| $\sigma$  | surface free energy, surface tension              |
| $w$       | mass fraction of condensable species              |

Subscripts:

|      |                            |
|------|----------------------------|
| $c$  | onset of condensation      |
| $cl$ | classical theory, Eq. (18) |
| $e$  | equilibrium                |
| $d$  | droplet                    |
| $l$  | liquid phase               |
| $o$  | initial or source          |
| $p$  | solid particle             |
| $s$  | saturation                 |
| $v$  | vapour phase               |
| $lv$ | liquid-vapour interface    |
| $sl$ | solid-liquid interface     |
| $sv$ | solid-vapour interface     |

Superscript:

|     |                  |
|-----|------------------|
| $*$ | critical cluster |
|-----|------------------|

## 1. INTRODUCTION

Nucleation and condensation phenomena are of fundamental importance in many fields such as atmospheric physics, astrophysics, aeronautical sciences, nuclear-reactor technology and the material sciences. They must be considered in weather prediction, aerosol formation, metallurgical techniques, high-speed wind tunnel design, steam-turbine nozzle design, rocket performance and high-intensity molecular beams. The processes include condensation of supersaturated vapour with or without foreign nuclei, crystal formation from vapour, melted and solid-liquid solutions, phase changes in solid states, crack nucleation in solids, and crystallization of polymers. Consequently, nucleation and condensation problems have been investigated intensively in recent years in diverse fields. The results of these studies were summarized by Hirth and Pound (1963), Zettelmoyer (1969, 1977) and Abraham (1974).

The formation and behaviour of condensed matter are controlled by microphysical processes which occur, in many cases, in heterogeneous phases. The microphysical mechanism by which nucleous atoms or molecules become activated and grow to larger size clusters is still poorly understood, especially for heterogeneous nucleation and condensation. Although homogeneous nucleation and condensation are not frequently found in nature and not very applicable to practical problems, the concepts established through the study of homogeneous nucleation and condensation provide a basis for understanding the physically more complicated process of heterogeneous nucleation and condensation. Much effort has been expended by many researchers in the quantitative understanding of homogeneous nucleation for over half a century.

Although it was an ambitious attempt to construct a theory for a nonequilibrium process like nucleation and condensation, the early investigators only managed to produce an approximate theory. Nevertheless, it succeeded in obtaining remarkable agreement with available experimental data. The theory connects equilibrium-rate distribution of clusters of near-critical size to the steady-state distribution of clusters. A very small cluster is assumed as a spherical drop of liquid. The free energy of the cluster is assumed to be equal to the free energy of the number of molecules in the bulk liquid plus the free energy due to the surface of the cluster. The supersaturated vapour is viewed as a mixture of ideal gas species, each species corresponding to a subcritical cluster of a given size. The equilibrium distribution of these clusters is then calculated. With an equilibrium-rate theory, the rate of nucleation can be predicted to be proportional to the equilibrium concentration of the cluster of critical size at which the free energy of the cluster is a minimum.

The crudeness of the calculation of the equilibrium distribution was recognized and improved using the more detailed methods of statistical mechanics. However, the classical theory still serves adequately in the interpretation of available experimental results except for the case of very high cooling rates as found in supersonic free-molecular jets. Since classical theory is based on a quasi-steady state nucleation concept, it becomes inapplicable when the time required to achieve steady-state nucleation is large compared with a characteristic time governing the change of state. In ordinary cloud chambers and nozzle flows, the characteristic



time of nucleation is generally too short to be accounted for. In rapid expansions of free-molecular and cluster beams it takes a longer time for the vapour to adjust to a steady-state than to pass through a nozzle. Further, classical theory assumes the free energy of formation of a critical droplet can be expressed in terms of the macroscopic surface tension of the bulk liquid and its volume free energy. In highly supersaturated situations, the critical nucleus may be exceedingly small, containing few molecules. Consequently, the macroscopic concepts of continuum thermodynamics become invalid.

In order to understand the nucleation mechanism of small clusters, theoretical studies were made from the standpoint of irreversible statistical mechanics by assuming intermolecular interactions between atoms or molecules and using molecular dynamics or Monte-Carlo methods. In order to solve the nonequilibrium process of nucleation, the kinetics of cluster formation were examined theoretically. In addition, the early stages of clusterization, especially dimerization, were investigated experimentally.

Nucleation and condensation processes in compressible flows are of importance in the aerospace sciences in designing supersonic and hypersonic wind tunnels and rocket nozzles. In turn, such flows provide fundamental data needed for an understanding of nucleation and condensation processes. The heat release due to condensation can be a significant flow disturbance. Consequently, the equations of motion with heat addition are solved and compared with experimental data to test the validity of different nucleation theories. In this respect, well-established flows in cloud chambers, supersonic nozzles and shock tubes have provided useful data in understanding macroscopic processes of nucleation and condensation. Reviews of such investigations were made by Wegener (1969, 1975 (a), (b), 1977).

Experiments with cluster beams in free-molecular jets have provided means of studying the material properties of small clusters. They also yielded fundamental insight into the kinetic process of nucleation. Most experiments on gas-phase nucleation in cloud chambers, continuum nozzle flows or rarefaction-wave flows were limited to finding the supersaturation ratios at which condensation occurs during an expansion. A quantitative interpretation of such experiments is hampered by the difficulty in accounting for small complex processes in terms of a simple result, say, in an integral form. To provide all the desired information about condensation, the ideal experiment would be the one in which the stepwise event from monomer to droplet could be observed. Molecular beam sampling of a free jet is capable of providing such information. A number of such studies have been done in this decade.

Fogs and clouds are very important phenomena of nucleation and condensation from a meteorological point of view. Similar phenomena on a smaller scale are experienced daily closer to home by using sprays, kettles, cigarettes or pipes. However, the mechanisms of nucleation and condensation in these cases are substantially different from those found in supersonic-nozzle flows, expansion waves and free-jet flows. Nucleation and condensation occur more heterogeneously. Liquid-soluble substrates or insoluble liquid-wet substrates mostly dominate the nucleation process. Physical and chemical surface characteristics of the substrates such as



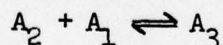
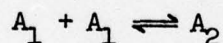
hydrophilicity, hydrophobicity, contamination, and surface catalyticity are much more important. Since the droplet size is usually of the order of  $1 \sim 100 \mu\text{m}$ , condensation is affected by more macroscopic features of the system such as turbulent coalescence, turbulent mixing and precipitation. Droplet growth is affected predominantly by the factors of continuum flow rather than those on the molecular level. Their features are too different to discuss them simultaneously.

In the present review, the subject matter is restricted to nonequilibrium flows with nucleation and condensation. Special emphasis is given to the theories of homogeneous nucleation and heterogeneous nucleation. The cited references are limited to those published since 1965. Unfortunately, it was not possible to include a comprehensive review of the Russian literature. Perhaps this will be done by Russian researchers in this field.

It should be noted that no claim is made for comprehensiveness. The field is just too large for that. Our modest aim was to provide a starting point for new researchers in this area. Neither is any claim made for a complete critical analysis of deficiencies in the various nucleation and condensation theories. Certainly the use of a correction factor for surface tension  $\sigma$ , condensation coefficient  $\alpha_c$  and others such as  $\Gamma$ , to try to fit experimental data is a very unsatisfactory procedure. Surer foundations will have to be laid in the future.

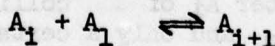
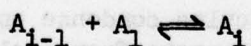
## 2. NUCLEATION

A vapour consists of clusters of molecules bound together by their intermolecular interactions. Nucleation from the vapour phase can be considered as a kinetic process that vapour molecules and their clusters combine with each other to form larger clusters (dimers, trimers, ..., i-mers). The elementary process may be expressed as a series of stepwise reactions consisting of bimolecular combination and unimolecular dissociation.



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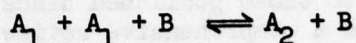
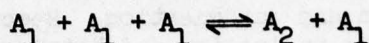
(1)



...

where  $A_1$  means a single vapour molecule (monomer) and  $A_i$  is a cluster containing  $i$  molecules of  $A_1$  ( $i$ -mer). Clusters  $A_i$  ( $i = 2, 3, \dots$ ) grow into  $A_{i+1}$  by addition of a single molecule through bimolecular combination (condensation) and decay into  $A_{i-1}$  by loss of a single molecule (evaporation) (Fig. 1). In addition to these processes, there may exist other processes

such as the formation of large clusters by the collision of two small clusters ( $A_i + A_j \rightarrow A_{i+j}$ ), the dissociation of large clusters into smaller ones ( $A_{i+j} \rightarrow A_i + A_j$ ), or three body reactions ( $A_i + A_j + A_k \rightarrow A_m + A_n$ ). However, these processes can be excluded as being too infrequent except the initial dimerization. It is recognized that the initial dimerization involves a third-body reaction (see Chapter 4.4) such as



where B means a single molecule of the third body (e.g., carrier gas). The phase change of condensation takes place when the growth process of combination dominates the decay process of cluster dissociation, thereby yielding increasing numbers of large clusters. Thus, if this multistate kinetics of clusterization is known, it is possible to calculate the time history of the concentration of clusters according to the rate equations subject to the initial conditions of clusters and the physical conditions of the system.

When only bimolecular reactions are taken into account, the number density of clusters of size  $i$ ,  $n_i$ , is given by solving the following equations:

$$\frac{dn_i}{dt} = I_i - I_{i+1} \quad (i \geq 2) \quad (2)$$

$$\frac{dn_1}{dt} = - \sum_{i=2} I_i$$

where  $I_i$  is the rate of formation of the  $i$ -mer given by

$$I_i = c_{i-1} n_{i-1} - e_i n_i \quad (3)$$

where  $c_{i-1}$  is the rate at which molecules condense on a cluster  $A_{i-1}$  and  $e_i$  is the rate at which molecules evaporate from a cluster  $A_i$  (Fig. 1). The vapour molecules strike a cluster  $A_i$  of the collision cross-section  $S_i$  with the mean molecular speed  $u_m$ , and only a certain fraction  $\alpha_c$  of these molecules sticks to the cluster. The condensation rate  $c_i$  is expressed as

$$c_i = \alpha_c u_m S_i \cdot n_1$$

According to the kinetic theory of molecular collision, the mean molecular speed can be given by  $(8kT/\pi m_{1,1})^{1/2}$  where  $T$  is the temperature,  $k$  the Boltzmann constant, and  $m_{1,1}$  the reduced mass of the cluster  $A_i$  and monomer  $A_1$  ( $= m/(i+1)$ ,  $m$  the mass of monomer). The collision cross-section  $S_i$  is



given by  $\pi r_1^2$  where  $r_1$  is the mean collision radius of  $A_1$  and  $A_1$ . Thus, when the vapour is an ideal gas ( $n_1 = p_v/kT$ ), the condensation rate is rewritten as

$$c_1 = \alpha_c 4\pi r_1^2 \frac{p_v}{\sqrt{2\pi m_{1,1} kT}} \quad (4)$$

Two particular states of the system can be specified; the steady case in which the concentration  $n_1$  does not change with time,  $dn_1/dt = 0$ ; and the quasi-equilibrium case in which the rate of cluster formation is zero,  $I_1 = 0$ , although, strictly speaking, an equilibrium state does not exist in a nucleation process. In the latter case, from Eq. (3)

$$\frac{e_1}{c_{1-1}} = \frac{n_{1-1,e}}{n_{1,e}} \quad (5)$$

where the subscript e denotes the equilibrium state. Small deviations of the  $c_{1-1}$  and  $e_1$  from the equilibrium values are assumed,  $c_{1-1,e} \approx c_{1-1}$ ,  $e_{1,e} \approx e_1$ . Thus, to predict the reaction rates  $c_1$  and  $e_1$ , it is required to know the statistical thermodynamic properties and the reaction cross-sections as a function of the relative kinetic energy of the reactants, their mutual orientation and the internal energy of rotation and vibration. Even with such knowledge available, it would be too difficult to derive an analytical formulation of a general nature for the exact calculation of the nucleation process except for dimer or trimer formation. For the latter cases, with steady progress in the understanding of intermolecular forces, it appears possible to develop such a rigorous kinetic theory. It is for these reasons that almost all existing (practical) nucleation theories bypass considering intermediate microscopic stages and adopt a thermodynamic or statistical approach in which only the initial and final stages are quoted without time dependence.

## 2.1 Statistical Thermodynamic Theory

The statistical thermodynamic theory of nucleation is a steady-state theory in which the concentrations of clusters are assumed to remain in a steady state:

$$\frac{dn_1}{dt} = 0 \quad (1 \geq 2)$$

with which Eq. (2) gives

$$I_1 = \text{const} = I \quad (1 \geq 2) \quad (6)$$

To maintain the system strictly in such a steady state, clusters must be removed from the system when they grow up to a certain terminal size  $i_\infty$ ,  $n_{i_\infty} = 0$ , and monomers are added to the system at the rate  $i_\infty I$ . From Eqs. (3) and (5), the rate of cluster formation  $I$  is related with the steady-state

concentration of clusters  $n_i$  and the equilibrium concentration of clusters,  $n_{i,e}$ ,

$$I = c_i n_{i,e} \left( \frac{n_i}{n_{i,e}} - \frac{n_{i+1}}{n_{i+1,e}} \right) \quad (i_\infty - 2 \geq i \geq 1)$$

$$= c_{i-1} n_{i,e} \frac{n_{i-1}}{n_{i-1,e}} \quad (i = i_\infty)$$

Summing the above equations divided by  $c_i n_{i,e}$  leads to

$$I = \left( \sum_{i=1}^{i_\infty-1} \frac{1}{c_i n_{i,e}} \right)^{-1} \frac{n_1}{n_{1,e}} \approx \left( \sum_{i=1}^{i_\infty} \frac{1}{c_i n_{i,e}} \right)^{-1} \quad (7)$$

Here, the reciprocal of the steady-state rate of cluster formation is equal to the sum of the reciprocals of all the equilibrium condensation rates of clusterization. This is a fundamental equation of nucleation rate which has been discussed by many investigators (Zettelmoyer, 1969, 1977). For clusters of large size, the discrete variables  $i$  in Eq. (7) are replaced by differentials to convert the summation to an integral form,

$$I = \left( \int_1^\infty \frac{di}{c_i n_{i,e}} \right)^{-1} \frac{n_1}{n_{1,e}} \quad (8)$$

Evaluation of the nucleation rate from Eqs. (7) or (8) requires knowledge of the condensation rate,  $c_i$ , and the equilibrium concentration of clusters,  $n_{i,e}$ . The former can be predicted by Eq. (4) from the molecular kinetics. By introducing the free energy of formation of clusters  $A_i$ ,  $\Delta G_i$ , the concentration of clusters in thermodynamic equilibrium can be expressed in the form

$$n_{i,e} = n_{1,e} \exp \left( - \frac{\Delta G_i}{kT} \right) \quad (9)$$

The free energy of cluster formation is equal to the elevation of the free energy for a transition from monomers to the cluster,

$$\Delta G_i = G_i - iG_1 \quad (10)$$

where  $G_1$  and  $G_i$  are the free energy of monomer and cluster, respectively. The free energy of the cluster can be determined a priori by combining quantum-mechanical, statistical-mechanical, and Monte-Carlo techniques, or it can be approximated in terms of the properties of the bulk material, being a function of cluster size.

Usually, the free energy of cluster formation,  $\Delta G_i$ , increases with the size of cluster, and is a maximum at some value of  $i$ , say  $i^*$ ,



at which

$$\left( \frac{\partial \Delta G_1}{\partial i} \right)_{i=i^*} = 0 \quad (11)$$

The cluster corresponding to the maximum value  $\Delta G_1$  is called "the critical nucleus or critical embryo", and has the lowest equilibrium concentration (Fig. 2). Once clusters achieve this critical size, the addition of another molecule to the cluster causes a decrease in the free energy of cluster formation. This means a high probability that they will grow to macroscopic size with relatively unhindered conditions. The value of  $\Delta G_1$  does not change very much with respect to  $i$  around  $i = i^*$ . Evaluating the integral in Eq. (8) by expanding  $\Delta G_1$  about its maximum with respect to  $i$  leads to an expression of  $I^*$  in the form

$$I^* \equiv I = Z_c c_i^* n_{i,e}^* = Z_c c_i^* n_{1,e} \exp \left( - \frac{\Delta G^*}{kT} \right) \quad (12)$$

where  $Z_c$  is known as the Zeldovich factor and given by

$$Z_c = \left\{ - \frac{1}{2\pi kT} \left( \frac{\partial^2 \Delta G_1}{\partial i^2} \right)_{i=i^*} \right\}^{1/2} \quad (13)$$

The nucleation rate given by Eq. (7) also can be reduced to the same form as Eq. (12) where the Zeldovich factor is given by

$$Z_c = \left( \sum_{i=1}^{\infty} \frac{c_i^* n_{i,e}^*}{c_i n_{1,e}} \right)^{-1} \quad (13a)$$

The expression of nucleation rate by Eq. (12) means that the steady-state rate of nucleation is equal to the equilibrium value with a correction factor  $Z_c$  which takes the value of  $10^{-1} \sim 10^{-2}$ .

The equilibrium concentration in Eq. (8) is dominated by the free energy of cluster formation,  $\Delta G_1^*$ , which depends on the statistical thermodynamic properties of clusters. Thus, the nucleation rate is predominantly controlled by this free energy. The quantitative estimation of the free energy of cluster formation is the major problem in quasi-steady nucleation theory. The physical reasoning and mathematical simplifications involved, such as nonequilibrium factors, choice of cluster partition function, re-evaporation, etc., provide a variety of additional effects. Recently, such statistical thermodynamics of nucleation was generalized by Derjaguin (1974).

## 2.2 Homogeneous Nucleation

The simplest description of the free energy of cluster formation is the liquid-drop model, often called the capillarity approximation, which has been used successfully for many years in the various areas of nucleation and condensation. The liquid drop model is based on a simple physical picture of the cluster. It is assumed that the cluster is viewed as a uniform spherical drop of liquid, which is basically bulk-like except for

the presence of the bulk-like surface. Thus, the free energy of formation of a droplet composed of  $i$  monomers is assumed to be equal to the sum of

- (i) the change in the free energy of  $i$  molecules from the vapour into the condensed phase, and
- (ii) the free energy of the generating surface on the bulk liquid in an amount equal to the surface area of the droplet,

$$\Delta G_i = i(\mu_l - \mu_v) + S_i \sigma \quad (14)$$

where  $\mu_l$  and  $\mu_v$  are chemical potentials per molecule in the equilibrium bulk-liquid phase and the supersaturated vapour at the pressure prevailing outside of the drop, respectively;  $\sigma$  the macroscopic interfacial free energy existing between the bulk liquid and the vapour (the surface tension), surface area of a sphere having a volume equal to  $i$  times the molecular volume  $v_{ml}$  in the bulk liquid phase,

$$S_i = 4\pi r^2 = 4\pi \left( \frac{3}{4\pi} i v_{ml} \right)^{2/3}$$

where  $r$  is the radius of the drop. A more generalized theory for non-spherical and anisotropic clusters was studied by Ziabicki (1968a, b).

The critical cluster is given by Eq. (11) with Eq. (14) as

$$r^* = \frac{2v_{ml}\sigma}{\mu_v - \mu_l} \quad i^* = \frac{8}{3} \pi \frac{\sigma}{\mu_v - \mu_l} r^{*2} \quad (15)$$

which gives

$$\Delta G^* = \frac{4\pi}{3} \sigma r^{*2} = \frac{16\pi}{3} \left( \frac{v_{ml}}{\mu_v - \mu_l} \right)^2 \sigma^3 \quad (16)$$

where the superscript  $*$  means the critical nucleus. The difference in chemical potentials is expressed as

$$\mu_v - \mu_l = kT \ln s \quad (17)$$

where  $s$  is the supersaturation or the ratio of the pressure of the condensable vapour  $p_v$  to the vapour pressure of the condensed phase (saturation pressure)  $p_s$ , or  $s = p_v/p_s$ . From Eq. (12) with Eqs. (4) and (16), the nucleation rate is

$$I^* = Z_c 4\pi r^{*2} \frac{\alpha_c p_v}{\sqrt{2\pi m kT}} \frac{p_v}{kT} \exp \left( - \frac{4\pi}{3} \frac{\sigma r^{*2}}{kT} \right) \quad (18)$$



This is the nucleation rate of the so-called classical (Becker-Döring) nucleation theory. The condensation coefficient is usually but unjustifiably assumed as  $\alpha_c = 1$ .

The Zeldovich factor is given by Eqs. (13) and (14)

$$Z_c = \left( \frac{\Delta G^*}{3\pi k T r^*} \right)^{1/2} = \left( \frac{\sigma v_m^2}{4\pi k T r^*{}^2} \right)^{1/2} \quad (19)$$

The factor usually is of the order of  $10^{-1} \sim 10^{-2}$ , being relatively insignificant compared with the remaining pre-exponential value in Eq. (18) of about  $10^{25}$ . A more exact prediction for this factor was studied by White (1969) using a steady-state random walk analysis. The usual expression for  $Z_c$ , Eq. (19), was found to be quite accurate.

The applicability and validity of the classical theory of nucleation are confined by the assumptions of steady-state, bulk thermodynamic properties and large cluster size. In ordinary cloud chambers, supersonic nozzle and shock tube flows, the relaxation time required to establish the steady-state concentration distribution of clusters is of the order of microseconds, while the characteristic time of change of the flow state extends to milliseconds. Here the steady-state assumption should be valid. On the other hand, in supersonic free-molecular jets, to be discussed in Section 4.4, the characteristic flow time is extremely small compared with the build-up time of steady-state nucleation. For such a situation, nucleation must be treated as a completely nonequilibrium process by solving a set of reaction equations (see Sections 2.4 and 4.4).

In Eq. (18), the concentration of monomers participating in the nucleation and condensation is assumed to be constant. However, in the process, the vapour molecules are consumed owing to nucleation and condensation and in time distributed to the associated clusters, or diffused away from the region of interest under nonuniform conditions in space. These effects were studied by Katz et al (1966), Katz and Blander (1973), Heist et al (1976), Ziabicki (1977), and Becker and Reiss (1976, 1977). In the associated vapour of distributed clusters, larger supersaturations are required for the same nucleation rate than that of the vapour containing monomers only, owing to the thermodynamic properties of the vapour rather than the kinetic formation process. Under the usual conditions in diffusion cloud chambers, the diffusion effect due to nonuniformities does not cause serious error.

In the exponential of Eq. (18),  $(\ln s)^2$  appears through  $r^*{}^2$ . Thus, the nucleation rate varies quite rapidly with supersaturation. It is this rapid variation of the nucleation rate which gives the "critical supersaturation", below which one can see nothing occurring and just above which nucleation suddenly occurs. The nucleation rate also depends very strongly on the surface tension as  $\sigma^3$ ; a 10% change in  $\sigma$  leads to changes in the nucleation rate by ten orders of magnitude. Thus, the correct values of these bulk properties are very important. Most of them are readily obtainable for common vapours from handbooks or with suitable extrapolations. The major uncertainty stems from the possible effect of drop size on the value of surface tension when the size is small. The



dependence of the surface tension on drop radius is expressed by functional forms like

$$\sigma = \frac{\sigma_{\infty}}{1 + \frac{a}{r} + \frac{b}{r^2}} \quad (20)$$

where  $\sigma_{\infty}$  is the surface tension acting on the flat surface of the condensate. However, there is no rigorous analysis which is suitable for condensation nuclei of 100 or fewer molecules of the complex liquid. Usually, the macroscopic flat-film surface tension  $\sigma_{\infty}$  is employed for nucleation rate calculation. An improved expression for the nucleation rate with macroscopic surface tension as a function of droplet radius was developed by Derjaguin and Prokhorov (1974).

Statistical-thermodynamic theory: From statistical mechanics the concentration of clusters of size  $i$  in chemical equilibrium is given by

$$n_{i,e} = Z_i \exp \left( \frac{i\mu}{kT} \right) \quad (21)$$

where  $Z_i$  is the partition function for a cluster of size  $i$  and  $\mu$  is the chemical potential of the monomer in the vapour. When the motion of the cluster is separated into translation of the whole cluster, rotation of the whole cluster, and internal motion of the molecules within the cluster, the partition function can be written as

$$Z_i = \sum_j Z_{\text{trans}}(i) Z_{\text{rot}}(i,j) Z_{\text{int}}(i,j)$$

where  $j$  represents distinguishable geometrical configurations of the cluster. The translational partition function,  $Z_{\text{trans}}$ , is independent of the cluster configuration. The rotational partition function,  $Z_{\text{rot}}$ , depends on the configuration only through the asymmetry of moments of inertia. The internal partition function,  $Z_{\text{int}}$ , requires complete knowledge of the cluster configuration. When Eq. (21) is compared with Eq. (9), it is seen that the free energy of cluster formation can be expressed in a different form from that of the drop model, Eq. (14). There are two approaches to improving the drop model in this way. The first is a hybrid approach which assumes basically the drop model with statistical mechanical corrections. The second is to evaluate directly the statistical mechanical formulation for the free energy, calculating the partition functions of clusters for all sizes which requires both a knowledge of the interaction potential of molecules of the cluster and suitable techniques of calculation such as molecular dynamics and Monte Carlo methods.

The first approach was initiated by G. M. Pound and his coworkers (the so-called Lothe-Pound theory) and by H. Reiss and his coworkers (the so-called Reiss-Katz-Cohen theory) (Zettlemoyer, 1977). The clusters in the vapour may behave dynamically like large gas molecules, having free translational and rotational motions. These motions contribute to the partition function of the cluster by factors which are equal to the translational and rotational partition functions as an almost rigid body,  $q_{\text{trans}}$

and  $q_{rot}$ , respectively. In order that the cluster has such motions in the vapour, certain motions of the cluster in the liquid bulk phase must be deactivated as it leaves the liquid bulk, since the total number of degrees of freedom of the cluster is conserved. The six degrees of freedom used in  $q_{trans}$  and  $q_{rot}$  can be compensated by introducing a "replacement factor"  $q_{rep}$  which is related to the internal partition functions of the cluster (Lothe and Pound, 1968). This leads to an increase in the pre-exponential of the nucleation rate given by the drop model in the form

$$I = \frac{q_{trans} q_{rot}}{q_{rep}} I_{cl} \quad (22)$$

where  $I_{cl}$  is the nucleation rate given by Eq. (18). Assuming that the six degrees of freedom of the cluster and the average degrees of freedom of the bulk liquid have the same partition function, Lothe and Pound (1966) estimated  $q_{trans} q_{rot}/q_{rep} \approx 10^{17}$  for water vapour nucleation. In view of the agreement with experimental result, this inconsistency was called the "translation-rotation paradox" by Reiss and Katz (1967). They considered that the centre of mass of a stationary drop fluctuates with high probability over a volume comparable to its physical volume. A partition function for this replacement motion nearly cancels the partition function for the motion of the centre of mass of the cluster in the vapour. Assuming the free energy of a drop created by removing a volume with fixed boundaries from the bulk liquid, Reiss, Katz and Cohen (1968) and Lin (1968) showed an increase in the nucleation rate of  $10^3 \sim 10^6$  for water, which decreases the predicted supersaturation only by  $8 \sim 10\%$ . Extensive discussions have appeared on this matter by Lothe and Pound (1966), Reiss and Katz (1967), Reiss, Katz and Cohen (1968), Lin (1968), Parlange (1968), Stillinger (1968), Abraham and Pound (1968), Lothe and Pound (1968), Cohen (1970), Reiss (1970, 1977), Kikuchi (1969, 1971, 1977), Nishioka et al (1971), Nishioka, Lothe and Pound (1972), Blander and Katz (1972) and Abraham (1974a), Reiss (1977), Nishioka and Pound (1977), Nishioka (1977), Miyazaki et al (1977). However, because of the current disagreement for a physical model of a cluster there is an extreme range in the value of  $q_{trans} q_{rot}/q_{rep}$  from  $10^0$  to  $10^{17}$ .

To resolve the disagreement between the experiments and the Lothe-Pound theory, Abraham (1969, 1974a) discussed the liquids studied in the experiments and features of their bulk surface structures such as liquid bonding characteristics, surface entropy, molecular dipole moment, acentric factors, and catalytic effects for condensation in ions. Hydrogen-bonded liquids are categorized into two classes of oriented polar molecules and non-oriented quasi-spherical molecules at the liquid surface. The former liquids follow the classical nucleation theory, whereas the latter liquids follow the Lothe-Pound theory. He suggested that the failure of the Lothe-Pound theory to explain the nucleation of polar liquids was due to its failure to account for the deviation of critical nucleus properties from bulk-liquid surface properties. If the dipole-dipole interaction energy of the highly oriented surface molecules is corrected for surface curvature, the surface free energy of the drop is appreciably greater than that predicted from the plane surface.

The classical model including the modified one mentioned above has many merits. It avoids the formidable problem of treating each cluster



on a molecular basis and relates the free energy of formation to measurable bulk properties. However, these properties, such as surface tension and surface area, have a questionable interpretation for clusters with less than 100 molecules and in addition the classical model has conceptual difficulties in its inability to uniquely relate terms in the statistical model to terms in the classical model (Eqs. 9 and 21). These difficulties can be avoided by a direct treatment of statistical mechanics of small clusters. This is the second approach to improving the drop model. For this purpose, a static technique has been employed by many investigators such as Abraham and Dare (1971a, b), Burton (1970, 1972, 1973), Dare et al (1972), Hale and Plummer (1974), Hoare and Pal (1971, 1975), Kistenmacher (1974), Lee et al (1973a), Nishioka (1971), and Plummer and Hale (1972). By assuming both an interaction potential between atoms and a structural model for the cluster, the harmonic oscillator partition function of the cluster is used to predict the thermodynamic properties. Although this procedure is very useful for studying small clusters in the solid phase, it is incapable of treating liquids because of the simultaneous assumption of interaction potential and structure configuration. The configuration of the cluster cannot be given independently of the interaction potential.

To assure this consistency, two mathematical methods are used: the molecular-dynamics method (McGinty, 1973) and the Monte Carlo method (Lee et al, 1973b). The molecular-dynamics method can provide both static and kinetic properties of cluster by calculating their time-averaged values. The Monte Carlo method gives their ensemble average, being restricted usually to static structural properties. The partition function is given by an integral of configuration probabilities with respect to all atoms or molecules of the cluster system. The configuration probability is a function of the total potential energy of the interaction between the atoms of molecules, which is determined by the interatomic or intermolecular potential. Thus, this method requires only a knowledge of the interatomic or intermolecular potential.

In molecular dynamics, the clusters are treated as molecules composed of spheres with assumed intermolecular potentials. The cluster partition functions are then evaluated from standard statistical-mechanics relations, using approximations such as the harmonic approximation for the vibrational partition functions and the rigid rotation approximation for the rotational partition functions. Each equilibrium cluster is found by relaxing the nonequilibrium cluster so that the potential energy of the cluster takes an extremum. From the partition function, thermodynamic functions for the system are then calculated, and the equilibrium concentration of clusters are obtained. Such molecular dynamic studies of microclusters were reported by McGinty (1973), Briant and Burton (1974, 1975a, b, 1976a, b), Kristensen et al (1974), and Zurek and Schieve (1978). The validity of such a molecular approach for cluster thermodynamics was studied by Courtney et al (1974).

In the Monte Carlo calculations, a large number of configurations are generated for a molecular cluster system in which the clusters are defined by a certain criterion. By assuming appropriate intermolecular potentials and canonically averaging with weighting of the obtained configurations corresponding to the associated potential energy, the thermodynamic properties of the cluster are calculated. Such calculations were performed by Lee et al (1973b), Abraham (1974a, b), Bonissent and Mutaftschiev (1974), Binder (1975), Müller-Krumbhaan and Stoll (1976), Kaelberer and Etters (1977), and Miyazaki et al (1977). Detailed considerations of the definition of physical clusters were recently given by Gill (1977) and Gill et al (1977).



Although these approaches rest on the conceptual exactness of the statistical-mechanical formulation of the free energy of cluster formation, the required knowledge of the intermolecular potential makes it difficult to perform the requisite calculations for arbitrary substances. Using an atomic model of clusters, Burton and Briant (1977) obtained universal correction factors,  $I_{\text{exact}}/I_{\text{cl}}$ , which were independent of the substance studied. The atoms were located on lattice points of a face-centred cubic lattice and interacted only through nearest neighbour bonds. Unlike Abraham (1969) who divided substances into the two categories mentioned above, they showed that for any substances at low supersaturation and low temperature, nucleation rates should be lower than those predicted by classical theory, while at high supersaturation and high temperature, higher nucleation rates should result. The features agree with observed data. However, to further validate the theory, many more experimental tests will be required over a wide range of supersaturation temperatures and liquids.

**Binary and multi-component mixtures:** Multi-component systems consisting of two or more substances of condensable vapour are very important for chemical engineering processes. Nucleation theories of the one-component system mentioned above can be extended to such multi-component systems. Hirschfelder (1974) extended Reiss' treatment of classical theory for a binary system to a multi-component system. Then the free energy of formation of a cluster of size  $i$  is given by

$$\Delta G_i = \sum_j i_j (\mu_{i_j} - \mu_{o_j}) + \sigma S_i \quad (23)$$

where  $\mu_{o_j}$  is the chemical potential per molecule of the  $j$ -th component in the vapour phase having the same composition as the cluster,  $\mu_{i_j}$  the chemical potential per molecule of the  $j$ -th component of the bulk material having the same phase and composition as the cluster,  $i_j$  the number of molecules of the  $j$ -th component in the cluster ( $i = \sum_j i_j$ ),  $\sigma$  the surface tension, and  $S_i$  the

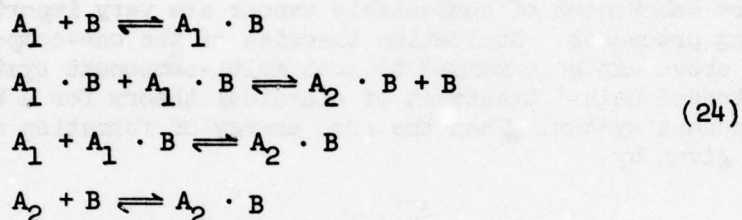
surface area of the cluster. In binary component systems, the point of unstable equilibrium for the critical nucleus corresponds to a saddle point on the free-energy surface of the composition plane.

Recent studies in this field were made by Mirabel and Katz (1974), Heist and Reiss (1974), Shugard et al (1974), Hirschfelder (1974), Wilemski (1975a, b), Takahashi et al (1975), Reiss et al (1976), Bouland (1977), and Wegener and Wu (1976). These theories make it possible to determine the value of the nucleation rate in relation to the partial pressures of the components. For binary sulfuric-acid water-vapour systems, even for humidities less than 100%, nucleation occurs at a low sulfuric acid partial pressure, because the mixture can be supersaturated with respect to the sulfuric acid solution (Heist and Reiss, 1974). Using rarefaction-wave flows of  $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$  binary system in a shock tube, Wegener and Wu (1976) observed a considerable reduction in the critical supersaturation of  $\text{C}_2\text{H}_5\text{OH}$  with increasing concentrations of  $\text{H}_2\text{O}$ . Wilemski (1975b) discussed the time lag needed to attain steady-state nucleation in binary vapours. Under certain conditions where the concentration of one of the two components is very small, the time lag may become so large that the classical theory of nucleation with the steady-state assumption is invalid. Comparisons between these theoretical and experimental studies do not always show good agreement due to the uncertainty of the vapour pressure and the nature of the resulting chemical compounds.

### 2.3 Heterogeneous Nucleation

Heterogeneous nucleation and condensation are more prevalent phenomena than homogeneous nucleation (Boucher, 1969, Sigsbee, 1969) in the cloud physics as well as in metallurgical fields. However, due to the complexity of its physical mechanisms and the difficulty of mathematical formulations, the systematic studies have made little progress to date. The main sources of heterogeneous nuclei in the atmosphere are smoke and vapour from fires and various industries, dust from land surfaces, salt from oceans, and particulate products from chemical reactions. The chemical and physical properties of these nuclei are extremely varied and complicated.

Heterogeneous nucleation and condensation can be characterized as nucleation under the existence of third bodies, B, which participate in the kinetic process as follows:



where  $A_i$  means an  $i$ -mer,  $A_i \cdot B$  an  $i$ -mer strongly combined with a third body B. Depending on the phase of the third body, heterogeneous nucleation and condensation are categorized into three types: B can be a (i) solid, (ii) liquid, or (iii) gas (molecule, atom, ion). The first means nucleation from the vapour on foreign solid particles. The monomer or  $i$ -mers are adsorbed onto or desorbed from the solid substrate. In the second case, they are dissolved into or absorbed into the liquid material depending on their solubility. Hence the process is dominated only by condensation (Saltanov and Tsirihin, 1977). The third case usually involves nucleation on ions and has been studied in some detail.

Nucleation on solid particles: The process of heterogeneous nucleation on solid particles is greatly influenced by geometrical, chemical and physical surface properties of the nuclei. Taking into account these features, several models have been proposed for heterogeneous nucleation from the macroscopic point of view (Hirth and Pound, 1963, Sigsbee, 1969, Boucher, 1969, and Zimmels, 1976).

Consider monomers of a supersaturated vapour impinging on the surface of a solid particle of radius  $R$ , to make a cap-shaped cluster embryo of radius  $r$ . There are two ways of monomer impingements on embryos: a direct impingement of monomers from the vapour and an impingement by desorption of adsorbed monomers (Fig. 3).

As for the homogeneous case, the equilibrium concentration of embryos of size  $i^*$  per unit surface area of substrate can be given by

$$n_{si,e}^* = n_{s1} \exp \left( - \frac{\Delta G^*}{kT} \right) \tag{25}$$



where  $n_{sl}$  is the concentration of adsorbed monomers on the substrate and  $\Delta G_i^*$  is the free energy of formation of an embryo of size  $i^*$  from the vapour phase monomer of concentration  $n_{sl}$ . The latter concentration can usually be expressed in terms of the impinging vapour monomer flux  $n_1 u_m$  and the mean monomer stay time on the substrate  $\tau$  as

$$n_{sl} = \alpha_a \tau \frac{p_v}{\sqrt{2\pi m k T}} \quad (26)$$

where  $\alpha_a$  is the adsorption coefficient and  $\tau$  is given by

$$\frac{1}{\tau} = \nu \exp \left( - \frac{\Delta G_d}{kT} \right) \quad (27)$$

where  $\Delta G_d$  is the desorption free energy of monomers and  $\nu$  is the vibrational frequency of the adsorbed monomer.

In the direct impingement process of vapour monomers, the impingement rate of monomers on the embryo is expressed as in Eq. (4),

$$C_{si}^* = a_v^* \frac{p_v}{\sqrt{2\pi m k T}} \quad (28)$$

where  $a_v^*$  is the surface area of the embryo. The nucleation rate per unit surface area of substrate in the form of Eq. (12) is then

$$I_s = Z_c a_v^* \frac{\alpha_a p_v}{\sqrt{2\pi m k T}} \frac{1}{\nu} \frac{p_v}{\sqrt{2\pi m k T}} \exp \left( \frac{\Delta G_d}{kT} \right) \exp \left( - \frac{\Delta G^*}{kT} \right) \quad (29)$$

In the impingement process of desorbed monomers, the rate at which desorbed monomers impinge upon the embryos on the substrate is given by

$$C_{si}^* = l_l l_s \frac{p_v}{\sqrt{2\pi m k T}} \tau \exp \left( - \frac{\Delta G_s}{kT} \right) \quad (30)$$

where  $l_l$  is the embryo perimeter,  $l_s$  the mean surface diffusion distance and  $\Delta G_s$  the free energy of activation for surface diffusion. The nucleation rate is then

$$I_s = Z_c l_l l_s \frac{\alpha_a p_v}{\sqrt{2\pi m k T}} \frac{1}{\nu} \frac{p_v}{\sqrt{2\pi m k T}} \exp \left( \frac{\Delta G_d - \Delta G_s}{kT} \right) \exp \left( - \frac{\Delta G^*}{kT} \right) \quad (31)$$

Using reasonable assumptions that  $\Delta G_s \ll \Delta G_d$  and  $l_l l_s \approx a_v^*$ , both nucleation rate equations can be expressed in the same form as

$$I_s = Z_c a_v^* \frac{\alpha_a}{\nu} \left( \frac{p_v}{\sqrt{2\pi m k T}} \right)^2 \exp \left( - \frac{\Delta G^* - n \Delta G_d}{kT} \right) \quad (32)$$



where  $n = 1$  for the direct impingement of monomers from the vapour, and  $n = 2$  for the impingement of desorbed monomers.

From the macroscopic surface-thermodynamic point of view, the critical free energy of the embryo formation can be expressed as the sum of contributions from the formation of the liquid bulk, the liquid-vapour interface, and the solid-liquid interface:

$$\Delta G_1 = \Delta G_b v_l + \sigma_{lv} a_v + (\sigma_{sl} - \sigma_{sv}) a_s \quad (33)$$

where  $\Delta G_b$  is the free-energy difference per unit volume of liquid phase from vapour to liquid phase being equal to  $(\mu_v - \mu_l)/v_{ml}$ ,  $\sigma_{ij}$  the surface free energy of the interface between phases  $i$  and  $j$ ,  $v_l$  the volume of liquid,  $a_v$  the surface area of liquid-vapour interface,  $a_s$  the surface area of liquid-substrate interface, and subscripts  $v$ ,  $l$  and  $s$  refer to vapour, liquid and substrate, respectively. From geometrical consideration,  $v_l$ ,  $a_v$  and  $a_s$  are written as

$$\begin{aligned} v_l &= \frac{4}{3} \pi r^2 a \left( \frac{r}{R}, \cos \theta \right) \\ a_v &= 4 \pi r^2 b_v \left( \frac{r}{R}, \cos \theta \right) \\ a_s &= 4 \pi r^2 b_s \left( \frac{r}{R}, \cos \theta \right) \end{aligned} \quad (34)$$

where  $a$ ,  $b_v$  and  $b_s$  are functions of  $r/R$  and the contact angle  $\theta$ .

By using the usual definition of the contact angle

$$\cos \theta = \frac{\sigma_{sl} - \sigma_{sv}}{\sigma_{lv}} = \frac{\sigma_{sl} - \sigma_{sv}}{\sigma} \quad (\sigma = \sigma_l) \quad (35)$$

and substituting Eqs.(34) and (35) into Eq.(33), the free energy of formation of an embryo of radius  $r$ , on a nucleus of radius  $R$ , can be expressed as a function of  $r$ ,  $R$  and  $\cos \theta$ . Differentiating  $\Delta G_1$  with respect to  $r$  to evaluate the critical free energy  $\Delta G^*$  gives the critical radius  $r^*$ ,

$$r^* = - \frac{2\sigma}{\Delta G_b} \quad (36)$$

The free energy of formation of a critical embryo is then

$$\Delta G^* = \frac{16\pi\sigma^3 v_{ml}^2}{3(kT \ln s)^2} f \left( \frac{r^*}{R}, \cos \theta \right) \quad (37)$$

where

$$f\left(\frac{r}{R}, \cos\theta\right) = \frac{1}{2} \left[ 1 + \left\{ c_\theta \left( \frac{r}{R} - \cos\theta \right) \right\}^3 + \left( \frac{R}{r} \right)^3 \left\{ 2 - 3c_\theta \left( 1 - \frac{r}{R} \cos\theta \right) \right. \right. \\ \left. \left. + c_\theta^3 \left( 1 - \frac{r}{R} \cos\theta \right)^3 \right\} + 3 \left( \frac{R}{r} \right)^2 \cos\theta \left\{ c_\theta \left( 1 - \frac{r}{R} \cos\theta \right) - 1 \right\} \right] \quad (38)$$

$$c_\theta = \left\{ 1 + \left( \frac{r}{R} \right)^2 - 2 \frac{r}{R} \cos\theta \right\}^{-1/2}$$

Due to the nature of the factor  $f(r/R, \cos\theta)$ , it is seen that lower values of contact angle reduce greatly the activation energy of critical embryo. Finally, the heterogeneous nucleation rate per unit area of nucleus substrate can be expressed as

$$I_s = I_o R_H \frac{\alpha_a^b}{\sqrt{f}} \sqrt{\frac{T}{T_o}} \exp \left\{ \beta_d \left( \frac{T_o}{T} - 1 \right) \right\} \exp \left\{ - \frac{4\pi}{3} \frac{r^*{}^2 \sigma}{kT} (f - 1) \right\} \quad (39)$$

where  $I_o$  means the homogeneous nucleation rate per unit volume of vapour,

$$I_o = Z_c 4\pi r^*{}^2 \frac{P_v}{\sqrt{2\pi m kT}} \frac{P_v}{kT} \exp \left( - \frac{4\pi}{3} \frac{r^*{}^2 \sigma}{kT} \right) \quad (39a)$$

and

$$R_H = \frac{1}{v} \sqrt{\frac{kT_o}{2\pi m}} e^{\beta_d}, \quad \beta_d = \frac{\Delta G_d}{kT_o} \quad (40)$$

**Nucleation on ions:** Clustering and condensation of vapour atoms or molecules on ions have been investigated since Wilson first demonstrated that ions enhance nucleation in cloud condensation. Ions provide a central force field, which is a simple form of attractive potential resulting in the formation of heterogeneous embryos. Therefore, a fundamental understanding of ion-induced nucleation would provide an important basis for further developments in the theory of heterogeneous nucleation. In an attempt to explain the process of nucleation about ions, several equations have been proposed by White and Kassner (1971), Mason (1971), Loeb (1971), Stachyorská (1965), Russel (1969), and Castleman and Tang (1972).

Gaseous ions attract vapour molecules to form small droplets in equilibrium with the vapour. A larger, single charged droplet may be formed by clustering the appropriate number of monomers to one droplet of radius  $r_a$ , containing  $i_a$  molecules (Fig. 4). The ion-field energy is changed due to surrounding dielectric molecules. By introducing an electrostatic term to account for the charge, the macroscopic free energy of embryo formation is written as

$$\Delta G_1 = \frac{4\pi}{3v_{ml}} (r^3 - r_a^3) (\mu_v - \mu_l) + 4\pi(r^2 - r_a^2) \sigma + \frac{1}{2} e^2 \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r} - \frac{1}{r_a}\right) \quad (41)$$

where  $\epsilon$  is the liquid dielectric constant and  $e$  is the electronic charge in Gaussian units. At  $r = r_a$ ,  $\Delta G_1 = 0$  and  $\partial \Delta G_1 / \partial r = 0$ , which means a metastable equilibrium. The first two terms consist of a term accounting for the free energy of vaporization of the condensing molecules and a surface term representing the work done in changing the surface area as a result of the condensation of additional molecules. The one additional term accounts for the change in the field energy about an ion owing to the condensation of a film of a given radius having a dielectric constant  $\epsilon$ . The dielectric constant of the surrounding vapour phase is generally taken to be close to unity.

The critical nucleus ( $\partial \Delta G_1 / \partial r = 0$ ) is then given by

$$\mu_v - \mu_l + \frac{2\sigma v_{ml}}{r} - \frac{e^2 v_{ml}}{8\pi r^4} \left(1 - \frac{1}{\epsilon}\right) = 0$$

which has two roots, the smaller one corresponding to  $r_a$  and the larger to  $r^*$ . The nucleation rate is then

$$I = Z_c 4\pi r^{*2} \frac{\alpha_c p_v}{\sqrt{2\pi m k T}} \frac{p_v}{kT} \exp \left( - \frac{\Delta G^*}{kT} \right) \quad (42)$$

where

$$\Delta G^* = \frac{4}{3} \pi \sigma (r^{*2} - r_a^2) + \frac{2}{3} e^2 \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r^*} - \frac{1}{r_a}\right) \quad (43)$$

and the Zeldovich factor is given by

$$Z_c = \left[ \frac{1}{9\pi k T r^{*2}} \left\{ 4\pi \sigma r^{*2} - \left(1 - \frac{1}{\epsilon}\right) \frac{e^2}{r^*} \right\} \right]^{1/2} \quad (44)$$

In this expression, only the term representing different ionic radii accounts for different ions, and it does not always predict observed variations in the nucleation rate when the sign of ions is changed. White and Kassner (1971) modified the term to account for dipole-dipole and dipole-quadrupole repulsions between the clustering molecules. In this manner, they arrived at a set of expressions for calculating numerical values of the free-energy barrier for nucleation about both negative and positive ions. The values appeared to be consistent with macroscopic observations of the relative saturation ratios required for nucleation about the respective ions of different sign.

Russell (1969) extended the homogeneous nucleation theory of Lothe and Pound to condensation on ions, taking the clusters as free particles and accounting for the corresponding partition functions. The free energy of



embryo formation is then expressed as

$$\Delta G_1' = \Delta G_1 - kT \ln \left\{ \left( \frac{q_{\text{trans}} q_{\text{rot}}}{q_{\text{rep}}} \right)_r / \left( \frac{q_{\text{trans}} q_{\text{rot}}}{q_{\text{rep}}} \right)_{r_a} \right\} \quad (45)$$

where  $q_{\text{trans}}$  and  $q_{\text{rot}}$  are molecular translational and rotational partition functions of the embryo taken as a rigid body, and  $q_{\text{rep}}$  is a constant term accounting for six internal degrees of freedom replaced by the translational and rotational motions. The last term is estimated as  $12kT \ln(r/r_a)$ , which leads to the nucleation rate

$$I' = \left( \frac{r^*}{r_a} \right)^{12} I \quad (46)$$

The factor  $(r^*/r_a)^{12}$  is of the order  $10^4$  in most cases. Both theories, Eqs. (42) and (46), are compared with cloud chamber measurements of rain limits, that is, the supersaturation needed to produce a rain of droplets. Neither theory predicted the different catalytic potencies of positive and negative ions.

All experimental studies of ion-induced nucleation have been made in cloud chambers, following exposure to high-energy X-rays or other suitable ionization sources, and measuring only macroscopic properties of droplet formation. Consequently, the molecular aspects of the phenomenon and especially the role of small clusters have remained obscure and many conflicting statements have appeared in the literature concerning the actual mechanisms involved. Mass-spectrometer techniques used with high-pressure ion-sources have yielded a wealth of information about clustering on ions. Water has received special attention. Clustering rates, equilibrium distributions, and other thermodynamic quantities have been determined for small-size clusters of water molecules on ions. In these studies, the classical liquid-drop model seems woefully unable to account for the properties of these small clusters, although it may be more realistic as clusters grow larger. For example, water does not condense around such ions as  $\text{O}_2^+$ ,  $\text{O}^+$ ,  $\text{N}_2^+$ ,  $\text{N}^+$ ,  $\text{Ar}^+$  or  $\text{He}^+$  as had been proposed. Instead, these ions rapidly react with water to form an equilibrium distribution of  $\text{H}^+(\text{H}_2\text{O})_n$ , which serves as a nucleus for further condensation. On the other hand, some ions such as  $\text{Pb}^+$ ,  $\text{Bi}^+$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  seem to form centres for clustering. Ion-molecule reactions are taking place during the course of the usual ion-induced nucleation experiment, generally leading to the formation of a complex group of ions of unknown composition.

To account for these features, the microcrystal statistical model developed for homogeneous clusters also can be applied to vapour-ion interactions. Casteman and Tang (1972) treated the clusters as harmonically-bound crystallites and calculated their partition functions directly on a high-speed computer. Once the partition functions are determined one can obtain detailed thermodynamic data for various cluster sizes over a wide range of pressure and a reasonable range of temperature. With the molecular dynamic method, Briant and Burton (1974) calculated the thermodynamic properties of the clusters consisting of one to four water molecules plus one ion and of four water molecules plus  $\text{NH}_3$ , assuming an effective potential for water-water and

water-ion interaction. O'Brien and Robinson (1974) also considered two sets of clusters of spherical shape and "grown" clusters of an ion plus different numbers (1 ~ 86) of molecules. Each cluster consists of Lennard-Jones (6-12) spheres (atoms or molecules) with a single charge ion in its centre. Mruisk et al (1974) applied the Monte Carlo method to a system of water vapour plus  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{F}^-$  ions for a cluster of one to six molecules of  $\text{H}_2\text{O}$ , and obtained sufficiently good agreement with experimental data.

## 2.4 Nonstationary Nucleation

In the case of condensation occurring in a vapour close to thermodynamic equilibrium, the features of the condensation process are not sensitive to the detailed cluster-formation model employed, and they are described by steady-state kinetics. However, a steady state can only be reached when all transient effects of the process have disappeared from the system. When this relaxation process takes a much longer time than the characteristic lifetime of the vapour system (as for a rapid expansion of supersonic free-molecular jets or in the associated vapour system) the transient processes play an important role in the clustering behaviour. For this purpose, nonsteady kinetics of clusterization must be considered.

Earlier approaches to this problem were reviewed by Courtney (1962). Employing the classical liquid-drop theory with a lower limit of applicability as a 19-molecule cluster and assuming a collision frequency for the rate constant, Courtney (1962) solved Eq. (2) and displayed the time dependence of concentrations of various size clusters ( $20 \leq i \leq 119$ ). Similar studies were done by Andres and Boundart (1965) and Abraham (1970, 1971) for  $11 \leq i \leq 110$ . The latter showed an overshoot of the current  $I_i$ , from the steady-state current  $I^*$ , for cluster sizes less than the critical size. The maximum overshoot is greater in magnitude and at an earlier time for small clusters. Kortzeborn and Abraham (1973) investigated the heterogeneous-nucleation problem of water monomers condensing onto a prescribed number of ions in a similar manner. In this case, the smallest cluster can be assumed to be in metastable equilibrium with a concentration equal to that of the ions. The time dependence of cluster concentration and current showed the same functional dependence as found in the homogeneous case. Firsch and Carlier (1971), Harstad (1975), Draine and Salpeter (1977) and Peak (1978) treated the system of cluster reactions as continuous in size to solve Eq. (2) in integral form and calculated the relaxation time, accounting for the effects of the concentration of the smallest cluster. Shugard and Reiss (1976) applied a stochastic approach to the non-steady nucleation process. The growth of droplets through the addition of simple molecules can be analogous to a random walk of walkers on a lattice of discrete size, where the number of molecules in a drop corresponds to the coordinate of the lattice. The developed theory was then applied to the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  vapour system, which had quite a long relaxation time in atmospheric conditions.

As mentioned above, in free-molecular jet-expansions, the kinetics of formation of increasingly larger molecular clusters is fundamentally necessary to characterize the condensation process. In this decade, extensive efforts have been made in this area, especially for dimer formation. This work will be described in Section 4.4 in connection with free-molecular jet flows. Recently, the kinetics of clustering was studied by Pouring (1977) and Kanyukhov and Faizulaev (1977) considering that decay and growth of clusters follow unimolecular and bimolecular reactions.



Pouring (1977) applied the cluster kinetic theory of Buckle (1969) to the condensation of water vapour in air. In the cluster theory, each cluster is an assembly of atoms bound by London forces. The probabilities of unimolecular and bimolecular reactions which control the decay and growth of clusters are determined from the phase integral for energy configurations. The internal energy in a cluster circulates freely between all degrees of freedom at some frequency. When the energy of a surface-site atom exceeds the coupling energy to its nearest neighbours, the atom is lost from the cluster. On the other hand, a cluster can grow only if the collision energy fails to dissociate the incipiently-bound atom from the site atom. To employ this cluster kinetics, he assumed molecular parameters, such as pair-interaction energy, cluster internal energy circulation frequency, surface-site to internal-site parameter, nearest-neighbour coordination numbers, monomer concentration, and cluster size of effective numerical infinity. After an initial equilibrium condition is established, the resulting relaxation process corresponding to changes in the thermodynamic state can be calculated by this kinetic theory. It was found that the nonequilibrium cluster behaviour is dominated by the behaviour of the internal energy redistribution frequency.

Zurek and Schieve (1978) used molecular dynamics to gain insight into the details of cluster formation. Molecules of a two-dimensional gas of hard-sphere well discs are placed initially on the regular lattice with equal speeds and random directions of motion. The initial condition for relaxation is produced by a few hundred collisions. Starting from this initial condition the evolution of the system is followed by investigating the temperature dependence of the mole fractions of small clusters formed in an adiabatically-isolated system. The topological aspect of clusters also was studied. The cluster tends to have, on the average, a much smaller number of bonds than the most compact configuration.

### 3. CONDENSATION

From the standpoint of nonsteady kinetic theory, condensation is a successive and continuous process of nucleation. However, in usual cases of condensation, the nuclei are considered to consist of a sufficiently large number of molecules that they form a liquid droplet. For such liquid droplets, it is convenient to analyse the process using macroscopic molecular dynamics or continuum dynamics.

#### 3.1 Droplet Growth

In the process of droplet growth, the molecular motion and the heat release by phase-transitions must be taken into account with appropriate boundary conditions on the droplet surface for incident and reflected vapour and gas molecules.

The transfer of mass, momentum and energy to droplets depends on the Knudsen number  $Kn = \lambda_m / r_d$ , where  $\lambda_m$  is the mean-free-path of the molecules in the gas and  $r_d$  the characteristic dimension of the droplet. The mean-free-path is given by

$$\lambda_m = \frac{3\sqrt{\pi}RT/\mu}{2p}$$



where  $\eta$  is the dynamic viscosity,  $R$  the gas constant and  $\mu$  the molecular weight. The limit of  $Kn \rightarrow 0$  corresponds to the continuum regime where the transport processes are governed by the usual fluid-dynamic equations. The mass flux of the vapour to a spherical droplet of radius  $r$  can be expressed as

$$\dot{m}_0 = 4\pi r^2 \frac{\rho_v D}{r} (C_{v\infty} - C_{vr})$$

where  $\rho_v$  is the density of the vapour,  $D$  the diffusion coefficient and  $C_{v\infty}$  and  $C_{vr}$  the concentrations of the vapour at infinity and at the droplet surface, respectively. The limit of  $Kn \rightarrow \infty$  corresponds to the free-molecular regime where the transfer processes are controlled by the interaction of individual gas molecules with the droplet. The mass flux of the vapour to the droplet is then given by the Hertz-Knudsen relation

$$\dot{m}_\infty = 4\pi r^2 m \left( \frac{p_v}{\sqrt{2\pi m k T}} - \frac{p_d}{\sqrt{2\pi m k T_d}} \right)$$

where  $m$  is the molecular mass,  $p_v$  the vapour pressure at the droplet surface, and  $p_d$  the saturation vapour pressure at the droplet temperature,  $T_d$ . The first term in the parentheses is the impingement rate of vapour molecule on the droplet surface, and the second is the evaporation rate.

In the intermediate regime, these expressions must be modified by an amount depending on the deviation from the foregoing limits. For a case slightly different from the free-molecular regime, a sticking coefficient,  $\alpha_c$ , is introduced, and the droplet growth rate can be expressed as

$$\frac{dr}{dt} = \alpha_c \frac{m}{\rho_l} \frac{p_v}{\sqrt{2\pi m k T}} \left( 1 - \frac{p_d}{p_v} \sqrt{\frac{T}{T_d}} \right) \quad (47)$$

where  $\rho_l$  is the density of liquid of the droplet. By introducing an effective condensation coefficient

$$\alpha'_c = \alpha_c \left( 1 - \frac{p_d}{p_v} \sqrt{\frac{T}{T_d}} \right) \quad (48)$$

Eq. (47) can be reduced to

$$\frac{dr}{dt} = \alpha'_c \frac{m}{\rho_l} \frac{p_v}{\sqrt{2\pi m k T}} \quad (47a)$$

The sticking coefficient  $\alpha_c$  is the ratio of the number of vapour molecules (or atoms) that become part of the liquid phase to the total number of molecules that impinge on the surface or the fraction of incident vapour-phase molecules which are trapped in the liquid-vapour surface potential-well after a single collision with the surface. The condensation coefficient is synonymous with the sticking coefficient. This concept and the concept of thermal accommodation coefficient form the basis of the equations for droplet growth in this regime.

Analytic expressions for droplet growth consider the diffusion of vapour toward the droplet and the conduction of heat away from the droplet. The sticking coefficient  $\alpha_c$  in the equation modifies the binary diffusion coefficient for the vapour diffusing through the noncondensing gas. The thermal accommodation coefficient  $\alpha_t$  modifies the thermal conductivity of the noncondensing gas. The latter coefficient is a measure of the efficiency with which the noncondensing gas removes heat from the droplet surface. In water-droplet growth as applied to the atmosphere, it appears reasonable to use an accommodation coefficient of unity. However, the sticking coefficient varies and depends on a number of factors such as the degree of contamination of the vapour and the nature of the noncondensing gas.

Values of the sticking coefficient can be obtained theoretically from kinetic theory by solving the Boltzmann equation in the vapour phase subject to the appropriate boundary conditions at the surface of the droplet. The solution can be expanded in terms of the inverse Knudsen number. The coefficients of this expansion are determined by collision integrals. This problem was studied by Kelly and Sengens (1972, 1974), and Loylka (1973) with a linearized BGK model.

Values of the sticking coefficient have also been obtained experimentally by several investigators for a variety of condensation and evaporation phenomena and experimental techniques. According to Mills and Seban (1967), the value ranged from 0.006 to unity. By means of thermal diffusion chambers, Chodes et al (1974), Gollub et al (1974) and Sinnarwall et al (1975) obtained an average value of 0.036. Vietti and Fastook (1976) measured water-droplet growth in air and CO<sub>2</sub> atmospheres using an expansion cloud chamber with a light scattering technique for saturation ratios  $s = 1.5 \sim 3.5$ . Comparing with the Fukuta-Walter theory (Eq. 53), they obtained a value of the sticking coefficient  $\alpha_c \approx 1$  for air and  $\alpha_c = 0.1 \sim 1$  for a CO<sub>2</sub> atmosphere ( $r < 2 \mu\text{m}$ ). For larger droplets in CO<sub>2</sub>, values smaller than 0.036 were observed. With a diffusion cloud chamber and a light scattering method, Gollub et al (1974) obtained values for the condensation coefficient and the thermal accommodation coefficient for small saturation ratios ( $s = 1.02 \sim 1.05$ ) as  $\alpha_t = 1$  and  $\alpha_c = 0.01 \sim 0.1$  for the  $3 \sim 7 \mu\text{m}$  radius range.

From continuum fluid-dynamics, several expressions are proposed for the droplet growth in the intermediate regime. When the droplet population is sufficiently low, the droplet and vapour system can be treated as a single droplet surrounded by an infinite vapour and noncondensable gas mixture. Gyarmathy (1963) considered mass and heat transfer about a liquid droplet of radius  $r$  in a mixture of the vapour and noncondensable gas, which lead to

$$T_r - T = \frac{\dot{m}L}{\xi_t 4\pi r^2} \quad P_v - P_{vr} = \frac{\dot{m}}{\xi_c 4\pi r^2} \quad P_{vr} = P_{sr} \exp \left( \frac{2\sigma}{\rho_v R_v T_r} \frac{1}{r} \right) \quad (49)$$

where  $\dot{m}$  is the condensation rate of vapour mass per unit time, being equal to  $d(4\pi/3r^3\rho_l)/dt$ ,  $T_r$  the surface temperature of the droplet,  $T$  the bulk gas temperature,  $p_{vr}$  and  $p_v$  the vapour pressure at the droplet surface and at infinity, respectively,  $p_{sr}$  the saturation vapour pressure at  $T_r$ ,  $\rho_v$  the density of the vapour,  $R_v$  the gas constant of the vapour,  $\sigma$  the surface tension,  $L$  the latent heat of vaporization, and  $\xi_t$  and  $\xi_c$  the transfer coefficients of heat and mass modified for the Knudsen flow:



$$\xi_t = \frac{\lambda}{r} \frac{1}{1 + a_t Kn} \quad \xi_c = \frac{D}{R_v T} \frac{p}{p_g} \frac{1}{r} \frac{1}{1 + a_c Kn} \quad (50)$$

where  $\lambda$  is the heat conductivity,  $D$  the binary diffusion coefficient,  $p$  the ambient pressure,  $p_g$  the pressure of the gas, and  $a_t$  and  $a_c$  are given by

$$a_t = \frac{4\sqrt{2\pi}}{\alpha_t} \frac{\gamma}{\gamma + 1} \frac{2\lambda}{3\eta c_p} \quad a_c = \frac{2\sqrt{2\pi}}{\alpha_{tv}} \sqrt{\frac{\mu_v}{\mu}} \frac{p}{p_g} \frac{2\rho D}{3\eta} \quad (51)$$

where  $\alpha_t$  and  $\alpha_{tv}$  are the thermal accommodation coefficients for the mixture and the vapour, respectively,  $\eta$  the dynamic viscosity,  $c_p$  the specific heat,  $\gamma$  the specific heat ratio,  $\rho$  the density of the mixture and  $\mu$  and  $\mu_v$  the molecular weights of the mixture and the vapour, respectively. From these relations and the Clausius-Clapeyron relation

$$\frac{dT_s}{dp_v} = \frac{RT_s^2 p_v}{L}$$

the droplet growth can be expressed as

$$\frac{dr}{dt} = \frac{\rho_l}{r} \left( 1 - \frac{r\sigma}{r} \right) \left\{ \frac{L^2}{\lambda RT^2} \frac{1}{1 + a_t Kn} + \frac{p - p_v}{p} \frac{R_v T}{p_v D} \frac{1}{1 + a_c Kn} \right\}^{-1} \ln \frac{p_v}{p_s} \quad (52)$$

where  $r\sigma = 2\sigma/(\rho_v R_v T) [\ln(p_v/p_s)]^{-1}$ . Employing this droplet growth law with the classical theory of homogeneous nucleation rate, Eq. (18), Barschdorff et al (1976) showed good agreement between the theoretical and experimental results in nozzle and shock-tube flows with condensation.

Fukuta and Walter (1970) derived a similar expression for the droplet growth law in the case of  $p_{v\infty} = 0$  ( $p_{g\infty} = p$ ), in which  $\alpha_{tv}$  in  $a_c$  is replaced by the condensation coefficient  $\alpha_c$

$$\frac{dr}{dt} = \frac{\rho_l}{r} \left\{ \frac{L^2}{\lambda RT^2} \frac{1}{1 + a_t Kn} + \frac{1}{\rho D} \frac{1}{1 + a_c Kn} \right\}^{-1} \left( \frac{p_v}{p_s} - 1 - \frac{r\sigma}{r} \right) \quad (53)$$

where

$$a_t = \frac{4\sqrt{2\pi}}{\alpha_t} \frac{\gamma}{\gamma + 1} \frac{2\lambda}{3\eta c_p} \quad a_c = \frac{2\sqrt{2\pi}}{\alpha_c} \frac{2\rho D}{3\eta} \quad (54)$$

Measuring the growth rate of water droplets in air, argon and helium atmospheres, in an expansion cloud chamber with a light scattering method, and comparing the results with various expressions of droplet growth, Vietti and Schuster (1973a, b) were not able to find a best fit for their data.

For densely populated droplets, the interactions between droplets must be taken into account due to the Brownian motion, electric charge and turbulent flow. In highly dispersed systems, coagulation due to the Brownian



motion as well as the environmental variation due to vapour depletion and heat release of condensation will predominate. On the other hand, turbulent flows will play an important role as the inter-droplet distances increase. The last effect was studied as an extension of a single droplet growth by Wagner and Pohl (1975) and Wagner (1975).

### 3.2 Condensate Mass

To calculate the flow variables, it is necessary to know the overall condensate mass as a function of time and space. For the nonsteady process of nucleation with a large relaxation time, the history of the condensate mass must be considered using nonsteady kinetic theory. For most systems with small relaxation times, it can be considered that liquid droplets with the critical radius are spontaneously nucleated corresponding to the vapour state and then grow to larger droplets obeying a growth law. Through vapour condensation, droplets nucleated at a time  $\tau$  with critical radius  $r^*(\tau)$  grow to droplets of radius  $r(t)$  at a time  $t$ . Since, during the time interval  $\tau$  to  $\tau + d\tau$ , the number of nucleated droplets is  $I(\tau)d\tau$ , the overall condensate mass per unit volume of the mixture at time  $t$  is written as

$$M = \int_0^t \frac{4\pi}{3} \rho_l I(\tau) r(t, \tau)^3 d\tau \quad (55)$$

The rate of production of the overall condensate mass is then

$$\dot{M} = \frac{4\pi}{3} \rho_l I(t) r^*(t)^3 + \int_0^t \frac{4\pi}{3} \rho_l I(\tau) \frac{d}{dt} \{r(t, \tau)\}^3 d\tau \quad (56)$$

When nucleation and condensation proceed heterogeneously on the surface of foreign solid or liquid particles, an additional contribution must be added to the above relation. In order to describe the number density and size distribution of such foreign nuclei, a distribution function with respect to the characteristic size of particles of an equivalent radius  $R$ , can be introduced. The distribution function  $N(R)$  multiplied by  $dR$  characterizes the number of particles lying in the size range  $R$  to  $R + dR$  per unit volume of vapour,

$$dN = N(R) dR \quad (57)$$

A nucleus particle has the surface area  $S_0$  at the initiation of nucleation. At time  $t$ , the area comes to be wetted by condensed droplets, say,  $S_g$ , and the surface area of a nucleus particle on which embryos can nucleate is then

$$S_e = S_0 - S_g \quad (58)$$

When the number-distribution function of foreign nuclei is  $N(R)$  and the nucleation rate per unit surface area of a nucleus particle is  $I_g$ , the total nucleation rate per unit volume of vapour is given by

$$I = \int_0^{\infty} I_s S_e N(R) dR = \int_0^{\infty} I_s (S_o - S_s) N(R) dR \quad (59)$$

The wetted surface area  $S_s$  is given by

$$S_s = \int_0^t I_s(\tau) (S_o - S_s) a_s(t, \tau) d\tau \quad (60)$$

where  $a_s(t, \tau)$  is the interfacial area between the nucleus particle and the condensate droplet which is formed at time  $\tau$  ( $< t$ ). The mass produced during the time  $\tau$  and  $\tau + d\tau$  is

$$\int_0^{\infty} I_s(\tau) (S_o - S_s) \rho_l v_l^* N(R) dR d\tau$$

and grows at time  $t$  up to

$$\int_0^{\infty} I_s(\tau) (S_o - S_s) \rho_l v_l(t, \tau) N(R) dR d\tau$$

where  $v_l$  represents the volume of the condensate. Thus, the overall condensate mass per unit vapour volume is given by

$$M = \int_0^{\infty} \left\{ \int_0^t I_s(\tau) (S_o - S_s) \rho_l v_l(t, \tau) d\tau \right\} N(R) dR \quad (61)$$

and the rate of production of the liquid phase by

$$\dot{M} = \int_0^{\infty} \left\{ I_s(t) (S_o - S_s) \rho_l v_l^* + \int_0^t I_s(\tau) (S_o - S_s) \tau \frac{\partial}{\partial t} (\rho_l v_l) d\tau \right\} N(R) dR \quad (62)$$

When condensation of the vapour takes place on the whole surface area of the foreign particle as in the case of liquid particles, it can be assumed that  $S_s = 0$  and  $S_o = 4\pi r^2$ .

Combining Eqs. (58) and (62) yields the final expression for the rate of production of the liquid phase as

$$\begin{aligned} \dot{M} = I(t) \frac{4\pi}{3} \rho_l r^{*3} &+ \int_0^t I(\tau) \frac{\partial}{\partial t} \left( \frac{4\pi}{3} \rho_l r^3 \right) d\tau \\ &+ \int_0^{\infty} \left\{ I_s(t) (S_o - S_s) \rho_l v_l^* + \int_0^t I_s(\tau) (S_o - S_s) \tau \frac{\partial}{\partial t} (\rho_l v_l) d\tau \right\} N(R) dR \end{aligned} \quad (63)$$



#### 4. FLOWS WITH NUCLEATION AND CONDENSATION

For a given initial condition of saturated or supersaturated vapour, a finite time is required for the molecules to achieve appreciable clusterization or critical nucleation. Such relaxation times of nucleation are of the order of microseconds (Andres, 1969). Thus, the vapour flow proceeds without condensation beyond the saturation state, being supercooled to a certain extent before the occurrence of observable nucleation (Fig. 5). In cloud chambers, supersonic nozzles, and shock tubes, the characteristic time of flow in which an appreciable change of the thermodynamic state occurs is of the order of milliseconds. The cooling rates of these flows usually obtained are shown in Table 1. For flows where the thermodynamic state changes sufficiently slowly compared with the kinetic process of clusterization, the kinetically steady state can be established after a very short induction time for nucleation, and the flow is described by a quasi-steady theory of nucleation. In such cases, nucleation and condensation can be regarded only as a heat-release process and the physical properties of the flow can be determined from well-established methods of gasdynamics. Consequently, such flows have been used for testing and understanding nucleation and condensation theories and to provide macroscopic theories of nucleation sufficiently useful for practical problems of condensation.

Under rapid expansions of free-molecular beams produced by expansion through an orifice or nozzle into high vacuum, the quasi-steady assumption of clusterization is no longer valid and a kinetic treatment must be used. In turn, the kinetic processes can be studied in such a flow system, and detailed information can be obtained on small clusters.

##### 4.1 Cloud Chambers

###### (i) Expansion Cloud-Chamber:

The cloud chamber commonly discussed by many investigators is the Wilson expansion chamber. Here, a mixture of vapour and inert carrier gas is expanded rapidly from a known initial volume to a known final volume under well-controlled conditions. The rapid expansion is usually obtained by actuating a piston or by opening a quick-acting valve to a lower pressure. The final state in the chamber is chosen to be supersaturated. By increasing the final supersaturation, the critical limit of supersaturation is determined beyond which the supersaturated state can no longer be sustained owing to onset of condensation. At this point, the nucleation rate per cubic centimeter per second is considered to lie in the neighbourhood of  $I = 1 \text{ drop}/(\text{cm}^3\text{s})$ .

For the study of homogeneous nucleation, the chamber is cleared of heterogeneous condensation nuclei by repeated expansion with the same mixture and removing the drops condensed on these nuclei. Possible condensation of vapour on ions is avoided by employing a suitable electric field and shielding the chamber against low-energy radiation. The critical supersaturation required for homogeneous nucleation is calculated by assuming that nucleation occurs at the maximum supersaturation achieved through expansion and assigning an appropriate duration time to this state - denoted as the sensitive time. Supersaturation, however, is continuously and rapidly varying with time, and additional nucleation and droplet growth are simultaneously and continuously occurring. The analysis of the results obtained by photographing the droplets



or from light scattering techniques must be studied using a nucleation-rate law and a droplet-growth law. A cloud chamber of this type for the study of homogeneous nucleation was developed to a high degree of refinement by Allard and Kassner (1965), and Kassner and Schmitt (1966). They used a programmed expansion - a large fast expansion followed by a small slow expansion and a small fast compression. The programmed expansion produces a roughly parabolic pulse of supersaturation. The small slow expansion offsets the increase in the temperature (decrease in supersaturation) of the interior gas of the chamber which is brought on by the heated boundary layers of the gas near the walls and/or around growing droplets. The small compression reduces the supersaturation to an extent so as to suppress the additional nucleation. At the same time, the supersaturation is kept high enough to insure rapid droplet growth. The pulse technique can provide sampling times which are considerably shorter than the natural "sensitive time" of the chamber. With photographic records of the total droplet population, which are taken after the droplets have grown to visible size, the relationship between nucleation rate and supersaturation is estimated in the following way. First, an empirical nucleation-rate versus supersaturation curve,  $I(s)$ , is assumed. The curve is integrated over the pulse shape of the experimental supersaturation to predict the droplet population.

$$n(t) = \int_0^t I(s) dt$$

The empirical curve  $I(s)$  is adjusted until the predicted value of the population agrees with the one obtained photographically. The final nucleation-rate versus supersaturation curve includes the effect of vapour depletion due to nucleation and droplet growth, which may not necessarily be considered in the nucleation theory. To avoid the latter effect, the sampling should be taken in an infinitesimally short time or the droplet growth by diffusion should be taken into account under the time-varying supersaturation owing to vapour depletion as well as continuous expansion or compression.

Such an attempt was made by Lund and Rivers (1966). They modified a droplet-growth law in cloud physics used by Fletcher and others for the growth and evaporation of cloud-chamber droplets. Using the classical nucleation theory and the droplet growth law, following the step-by-step growth of droplets and correcting nominal supersaturations obtained from pressure records for vapour depletion, they predicted droplet-population and droplet-size in reasonable agreement with observations. However, an exact treatment of this problem is complicated by the necessity of solving the nonsteady equations of heat and mass transfer with moving boundary conditions which are time-dependent. For this purpose, the technique used for a shock-tube rarefaction-wave flow can be employed (see Section 4.3)

In addition to such nonstationary processes, the results obtained from an expansion cloud-chamber depends on the degree of adiabaticity of the apparatus, size of the chamber, "sensitive time" of expansion, and observation techniques. These complexities have been circumvented by the development of the diffusion cloud-chamber.

#### (11) Diffusion Cloud-Chamber

During the past decade, Katz and his coworkers (1967, 1970a, 1975, 1976) have refined the thermal-diffusion cloud-chamber to such an extent that

the chamber is now one of the best quantitative methods for studying the nucleation process in a gas. As shown in Fig. 6, it consists of a warm bottom plate and a cooler top plate. A pool of working fluid under investigation covers the lower plate. The space above the pool is filled with a light, inert gas such as helium. The side walls of the chamber form a cylinder and can be constructed of glass, quartz or other materials containing windows through which optical observations can be made. Vapour evaporates from the surface of the pool and diffuses to the upper plate where it condenses at lower temperatures. The upper plate is slightly beveled and the condensate flows to the side walls where it returns to the lower pool. The total density of the vapour-carrier-gas mixture decreases from the bottom to the top to prevent natural convection. Since the saturation vapour pressure of the mixture varies exponentially with temperature and the partial pressure of the vapour is nearly linear, a supersaturated state can be obtained through the chamber. At given temperatures of the upper and lower plates, a steady state is set up in which supersaturation passes through a maximum at a point relatively distant from either plate. In order that the distribution of temperature and supersaturation in the chamber should be easily predicted, the chamber must be designed to produce, to a high degree of approximation, one-dimensional diffusion of heat and mass and it must always operate under conditions in which very few droplets form.

A single experiment consists of setting the temperature gradient such that the chamber is visually observed to be nucleating at a rate of about  $2 \sim 3 \text{ drops cm}^{-3} \text{ sec}^{-1}$  and then measuring the total pressure and the temperatures at the surface of the evaporating pool and at the top plate. The temperatures of both plates are then decreased or increased and the experiment is repeated in such a way that the same rate of nucleation is always observed. The critical supersaturation at a given temperature, the supersaturation which just initiates nucleation at the assigned rate (of  $1 \sim 10 \text{ droplets cm}^{-3} \text{ sec}^{-1}$ ) can be obtained as the envelope of the individual supersaturation curve plotted versus the temperature for each experiment (Fig. 7).

Using this technique, Katz and his coworkers carried out an extensive study to determine the critical supersaturations for homogeneous nucleation of various substances such as ethanol, methanol, n-hexane and water in the temperature range 235 to 295 K (1967), n-hexane, n-heptane, n-octane and n-nonane in the temperature range 225 to 330 K (1970a), benzene, toluene, o-xylene and n-butylbenzene over as much as a 150 K-range of temperatures (1975), and carbon tetrachloride ( $\text{CCl}_4$ ), chloroform ( $\text{CHCl}_3$ ), Freon 11 ( $\text{CCl}_3\text{F}$ ) and 1-1-2-2-tetrachloro-ethane ( $\text{C}_2\text{H}_2\text{Cl}_4$ ) over as much as a 90 K-range of temperatures (1976). The results obtained were compared with predictions from homogeneous nucleation theories. The classical theory, Eq. (18), was found to be in excellent agreement without any correction for the dependence of surface tension on radius even at radii as small as  $9.7 \text{ \AA}$  containing 16 molecules of n-butylbenzene at 215 K or  $11.7 \text{ \AA}$  containing 24 molecules of n-nonane at 230 K. However, in shock tube flows where the particle radius is less than  $10 \text{ \AA}$ , it was necessary to "adjust" the values of surface tension for a good fit of analysis with experiment (Sislian, 1976 and Sislian and Glass, 1977). The results for chloroform and Freon 11 obtained with a supersonic nozzle showed a good agreement with the Lothe-Pound theory, Eq. (22) (Jaeger et al, 1969, Dawson et al, 1969). However, now the results from a diffusion chamber were found to be in very good agreement with classical theory, Eq. (18). By using hydrogen, helium, neon, nitrogen and argon as the



carrier gas, the effects of quantities and species of carrier gas were also studied. As long as the total pressure was greater than about 2.5 times the equilibrium vapour pressure at the top of the bottom plate, the amount of carrier gas was found to have no effect on the observed critical supersaturation.

The experimental data for water vapour obtained by Katz and Ostermier (1967) exhibited considerable scatter by comparison with their other results. Keist and Reiss (1973) considered that this arose because the water which condensed on the top plate did not wet the metal surface but formed large drops which fell through the chamber to make disturbances. By covering the top plate with a thin layer of Pyrex glass wool so that water wetted the glass wool to drain to the side walls, they succeeded in eliminating the scatter and obtained reliable data for homogeneous nucleation of water. In this case, the classical nucleation-theory provided excellent agreement with experimental results. It should be noted that, by contrast with nozzle and shock-tube flows, almost all the results from cloud chamber are in good agreement with the classical droplet-model theory. At present, it is not clear whether this is due to the physical features of cloud chamber or to the limited experimental conditions.

The diffusion cloud-chamber has the following advantages: (a) it is a steady-state device such that a stationary state of a specified nucleation rate can be used to determine the critical supersaturation; (b) the chamber is self-cleaning. Once a dust particle has nucleated a droplet, it rapidly grows to visible size and falls into the liquid pool; (c) the chamber effectively has no walls; (d) nucleation on ions or those caused by the passage of an energetic particle are readily distinguishable from homogeneous nucleation. However, its applicability is limited by the following factors: (i) the substance to be studied must be liquid, with the temperature below the critical point and above the triple point, at both the bottom and top plates; (ii) the heat and mass transfer equations require an accurate knowledge of the thermal conductivity and the diffusion coefficient of the vapour-carrier-gas mixture as a function of both temperature and composition.

The diffusion cloud chamber, however, because of its advantages, can be used for other studies such as nucleation on ions, in binary or multi-component systems. Furthermore, the nucleation and growth processes have the possibilities of being applied to the detection and amplification in chemical-physical phenomena involving neutral molecules. Reiss et al (1977) have uncovered many experimental difficulties in adapting the diffusion chamber for this purpose but nevertheless obtained some quantitative results.

#### 4.2 Nozzle Flows

Nucleation and condensation in nozzle flows are important in connection with the design and performance of supersonic and hypersonic wind tunnels, rocket nozzles, steam turbines, and cooling towers. Extensive theoretical and experimental studies have been reported since Stodola in 1927. As a result, nozzle condensation is now understood in some detail. Recently, the nozzle-flow technique was applied successfully to studies of homogeneous-nucleation and condensation problems. Some favourable features of nozzle-flow experiments are that (a) the state is steady so that the entire history of expansion is readily obtained, (b) the flow between the wall boundary layers may generally be considered as a uniform adiabatic flow, (c) nucleation is



unlikely to occur in the boundary layers since these are largely superheated due to friction effects, (d) the rate of condensation can be estimated by measuring wall static pressures. A good review of the subject was given recently by Wegener (1969, 1975, 1977), where relevant previous papers up to 1976 are listed.

When a vapour or vapour mixture flows along the axis of a supersonic nozzle, the vapour pressure decreases with decreasing temperature more rapidly than the expansion pressure down to or below the saturation pressure. Further expansion may lead to condensation, which causes first a slight deviation of static pressure from the isentropic expansion and then an almost abrupt increase in the pressure in a short distance (Fig. 8). In this condensation zone, the maximum heat release is attained. Further expansion leads to two-phase flow of an asymptotically saturated vapour and liquid droplets. Depending on prevailing stagnation conditions, nucleation and condensation can also occur in subsonic nozzles (Barschdorff et al, 1976).

Typical nozzles used for condensation studies (except free-molecular beams) have high Reynolds numbers  $10^4$  to  $10^6$ . Therefore, viscous effects are negligible and the boundary layers are confined to a very thin region close to the walls. In addition, owing to negligible wall curvature one can obtain a uniform velocity distribution across the cross-sections. For such flows at high Reynolds numbers and low supersonic Mach numbers, the concepts of one-dimensional inviscid continuum flow are applicable. Employing this assumption, Hill (1966) showed that the features of condensation flows in a nozzle were well-predicted by the gasdynamic equations when coupled with the classical nucleation theory.

For a mixture of a condensible vapour, its liquid condensate, a noncondensable inert gas and foreign liquid or solid particles (suffixes v, l, g and p), the equations of mass, momentum and energy are:

$$\frac{d}{dx} (w_v + w_l) = 0 \quad (64)$$

$$\frac{d}{dx} \{ (w_v + w_g)u + w_l u_l + w_p u_p \} + \frac{dp}{dx} A = 0 \quad (65)$$

$$\frac{d}{dx} \left\{ w_v \left( h_v + \frac{u^2}{2} \right) + w_g \left( h_g + \frac{u^2}{2} \right) + w_l \left( h_l + \frac{u_l^2}{2} \right) + w_p \left( h_p + \frac{u_p^2}{2} \right) \right\} = 0 \quad (66)$$

with  $w$  - mass-flow rate,  $u$  - one-dimensional axial flow velocity,  $p$  - pressure,  $h$  - enthalpy and  $A$  - cross-sectional area of the nozzle. The cross-sectional area is adjusted by a small empirical correction for the boundary-layer effect.

When the no-slip condition of velocity and temperature between the gas, the condensate and the particle applies, the equations can be reduced to simple inviscid one-dimensional form:

$$\frac{d}{dx} (\rho u A) = 0$$

$$\rho u \frac{du}{dx} + \frac{dp}{dx} = 0 \quad (67)$$

$$\frac{d}{dx} \left( \frac{1}{2} u^2 + c_{p0} T - gL \right) = 0$$

where the density  $\rho$  and the specific heat  $c_{p0}$  are defined by

$$\rho = \rho_g + \rho_v + \rho'_l + \rho'_p \quad (68)$$

$$c_{p0} = (1 - \omega_0 - g_p) c_{pg} + \omega_0 c_{pv} + g_p \frac{h_p}{T}$$

with  $\rho'_l$  and  $\rho'_p$  as the mass of the condensate (=M) and the foreign particles per unit volume of the mixture, respectively;  $c_p$  - specific heat at constant pressure,  $L$  - latent heat of vaporization of the liquid, and

$$\omega = \frac{\rho_v + \rho'_l}{\rho} (= \omega_0) \quad g = \frac{\rho'_l}{\rho} = \frac{M}{\rho} \quad g_p = \frac{\rho'_p}{\rho} \quad (69)$$

$\omega$  is the mass fraction of the condensable vapour and the condensate - a constant throughout the expansion;  $g$  and  $g_p$  are the mass fraction of the condensate and the particles, respectively. The presence of the term  $gL$  in the energy equation means that vapour condensation is equivalent to a heat addition per unit mass of the flow.

The equation of state can be written as

$$p = \left( \frac{1 - \omega_0 - g_p}{\mu_g} + \frac{\omega_0 - g}{\mu_v} \right) \rho RT \quad (70)$$

where  $\mu$  is the molar weight. For certain fluids, say high-pressure steam or metal vapour, the equation of state may deviate from an ideal gas and must be expressed in a more complex form.

The mass fraction of condensate is given by Eq. (55),

$$g(x) = \int_{-\infty}^x \frac{4\pi}{3} \rho_l I(\xi) r(x, \xi)^3 \frac{d\xi}{\rho(\xi) u(\xi)} \quad (71)$$

For the nucleation rate  $I(\xi)$ , Eq. (18) can be chosen practically as a basis for modification to Eq. (22). The early stage of droplet growth after nucleation takes place under free-molecule-flow conditions due to the small cluster size. The droplet growth rate then is given by Eq. (47a).



The set of equations, Eqs. (67) to (71), subject to stagnation conditions completes the gasdynamic description of the flow with condensation. The integration of these equations along a streamline, i.e., the nozzle axis, gives the flow variables,  $\rho$ ,  $u$ ,  $p$ ,  $T$  and  $g$  (Fig. 9). Provided that the pressure ratio across the nozzle is enough to produce sonic flow at the throat and that thermal choking due to heat release of condensation does not occur, the integration is rather straightforward. When one of the variables such as the static pressure  $p(x)$  is measured and known, one of the remaining variables, e.g., the mass fraction of condensate  $g$ , can be predicted by these equations. To test the nucleation-rate equation or the droplet-growth law, the predicted variable must be compared with the measured one. Alternatively, the critical supersaturation, which is estimated from the behaviour of the condensate mass, can be compared with the value calculated using the nucleation-rate equations.

Employing this method with measurement of the static pressures for vapours of  $H_2O$ ,  $C_6H_6$ ,  $CHCl_3$ ,  $CCl_3F$  and  $C_2H_5OH$  expanding in a supersonic air nozzle ( $w_0 = 0.04 \sim 0.2$ ), Jaeger et al (1969) and Dawson et al (1969) concluded that the nucleation rates in vapour of regular-shaped, non-polar molecules ( $NH_3$ ,  $C_6H_6$ ,  $CHCl_3$ ,  $CCl_3F$ ) were in quantitative agreement with the Lothe-Pound theory, Eq. (22), while fluids having hydrogen bonding or rod-shaped molecules ( $H_2O$ ,  $C_2H_5OH$ ) tended to follow the classical theory, Eq. (18). The condensation coefficients were estimated from the shape of the pressure profile as being between 1 and 0.1 for the former fluids ( $NH_3$ ,  $C_6H_6$ ,  $CHCl_3$ ,  $CCl_3F$ ) and between 0.1 and 0.01 for the latter ( $H_2O$ ,  $C_2H_5OH$ ). The orientation of molecules at the cluster surface is considered to cause these features (see Section 2.2).

On the other hand, Wegener et al (1972) measured the static-pressure distribution on the centreline of the supersonic nozzle flow of ethanol-air (or nitrogen) mixture with a hypodermic tube, and examined a correction factor to the classical nucleation theory by introducing the factor  $\Gamma$  in the expression of the nucleation rate

$$I = \Gamma \cdot I_{cl} \quad (72)$$

where  $I_{cl}$  is given by Eq. (18). Since the critical radii of the clusters are appreciably smaller than those observed in cloud chambers owing to higher cooling rates, the effect of droplet radius on the surface tension must be taken into account in  $I_{cl}$ . The factor  $\Gamma$  can be written in the Lothe-Pound expression, Eq. (22),

$$\Gamma = \frac{q_{trans} q_{rot}}{q_{rep}} \equiv \Gamma_{LP} \quad (73)$$

By calculating the steady-state rate of nucleation, the replacement factor  $q_{rep}$  and the effective surface tension were determined so as to match the observed condensation. A value for  $\Gamma$  can be chosen for which the rapid increase in calculated nucleation rate coincides with the observed onset of condensation (Fig. 9). When the surface tension takes the value for a flat surface  $\sigma_{\infty}$ , the experiment yields  $q_{rep} \sim 10^{14}$  and  $\Gamma \sim 10^5$  for  $w_0 = 0.05$ . If smaller values of surface tension are chosen for smaller droplets,  $q_{rep}$  becomes larger than  $10^{14}$  and  $\Gamma$  approaches unity; for  $\sigma/\sigma_{\infty} \approx 0.8$ ,  $q_{rep} \sim 10^{18}$  and  $\Gamma \approx 10$ . A combination of the nucleation rate with these values of  $q_{rep}$  and  $\sigma$  and the droplet-growth

law with a suitable condensation coefficient ( $\alpha_c = 0.7$ ) permits the calculation of the condensate mass fraction to fit the experimental results (Fig. 9). Although the Lothe-Pound factor  $\Gamma_{LP}$  is not directly applicable to liquid, its values ( $\Gamma_{LP} \approx 10^{17}$ ) are appreciably above those from experiments.

Wu et al (1977) studied condensation of sulfur hexafluoride ( $SF_6$ ) carried in argon and obtained the values of  $10^4 \lesssim \Gamma \lesssim 10^5$  for  $0.37 \gtrsim \omega_0 \gtrsim 0.01$ . As mentioned later, using rarefaction waves in a shock tube for water vapour condensation in carrier gases of He, Ar and air and comparing the results with the non-isothermal classical theory, Eq. (74), Barschdorff (1975) obtained  $10^4 \lesssim \Gamma \lesssim 10^6$  for  $1 \gtrsim \omega_0 \gtrsim 0.004$ . Wegener and Wu (1976, 1977) compared these experiments and showed the values of  $\Gamma$  for various vapours (Table 2). All data exhibit higher nucleation rates of several orders than those predicted by the classical theory. It is interesting to compare these results of nozzle flows  $\Gamma \gg 1$  with those of cloud chambers  $\Gamma \approx 1$ , although the reasons for such large variations remain to be solved. The factor  $\Gamma$  must be considered as a correction factor for the classical homogeneous-nucleation rate to account for both contributions from statistical-mechanic and thermodynamic sources and from other uncertainties. The latter may arise from the possible non-homogeneous nucleation caused by impurities and flow properties.

In pure-vapour condensation, some of the vapour molecules colliding with droplets must act as a carrier of the thermal energy from the latent heat condensation. Thus, the simplifying condition of equal temperatures for droplets and vapour ceases to be valid, and the classical isothermal theory will predict considerably higher condensation rates or smaller values of  $\Gamma$ . Introducing a correction factor for the non-isothermal removal of latent heat from condensate clusters  $\xi$ , Barschdorff et al (1971, 1976) and Ludig (1975) modified Eq. (72) for wet steam,

$$I = \xi \Gamma I_{cl} \quad (74)$$

The factor  $\xi$  as derived by Feder et al (1966), is

$$\xi = \frac{\gamma + 1}{(\gamma + 1) + 2(\gamma - 1) \left\{ \frac{\mu L}{RT} - \frac{1}{2} - \left( 1 - \frac{\partial \ln \sigma}{\partial \ln T} \right) \ln s \right\}^2} \quad (75)$$

Comparing the calculated pressure distribution with the measured pressure profile, they obtained the best-fit values for the factor  $\Gamma$  for a number of steam experiments from several investigations. The result showed that classical nucleation theory with a correction factor  $\xi$ , a bulk-liquid surface-tension and a thermal-accommodation coefficient of unity predict well the experimental results for low initial stagnation pressures ( $< 0.5$  bar). For higher pressures, the values of  $\Gamma$  decrease up to about  $\sim 10^{-5}$  at 5 bar. Saltanov et al (1971) introduced a correction factor  $\beta$  for nucleation work into the exponent as  $\exp(-\beta \Delta G^*/kT)$  and compared the predicted and experimental results of steam. The factor increases with the stagnation pressure, taking values between 2.5 and 5 in the range of  $1 < p_0 < 32$  bar. This also means smaller values of  $\Gamma$  at higher pressures. Although quantitatively unexplained, one of the main reasons for this discrepancy can be attributed to the use of a perfect-gas equation of state. A real-gas equation reduces the nucleation rate considerably



(Bier et al, 1977). Real-gas analyses were made by Ludig (1975), Puzyrewski (1975), Puzyrewski and Studzinski (1977) and Bier et al (1977).

When coagulation of droplets is neglected, the number of droplets can be compared directly with the measured value. The former is given by

$$n(x) = \rho(x) \int_0^x \frac{I(\xi)}{\rho(\xi)u(\xi)} d\xi \quad (76)$$

The latter can be obtained by means of light-scattering methods (Stein and Wegener, 1967; Stein, 1969; Clumpner, 1971; Stein and Moses, 1972; and Conard, 1977). By this technique, Stein and Wegener (1967) found agreement for water vapour with the classical nucleation-rate theory using properties of ice and a condensation coefficient of unity. Using an ethyl alcohol-vapour air mixture, Clumpner (1971) studied the number and size of droplets in the liquid state leaving a supersonic nozzle exit and showed a narrow distribution of droplet radius about a mean size. This implies that most of the droplets formed in a narrow range of locations close to the peak value of the nucleation rate.

In actual nozzle flows, two-dimensional flow conditions between the nozzle axis and the wall exist which yield different cooling rates. Such supersonic-nozzle flows with condensation were studied by Davydov (1972), Tkalenko (1972) and Bratos and Jaescke (1974) using the method of characteristics. The results show that condensation occurs at the wall further upstream than at the axis. The pressure, temperature and density deviate more strongly from the isentropic values along the axis than the wall. Also the distributions of droplet size are significantly different along the axis and the wall. These aspects well describe the experimental results, although the effects of two-phase turbulent motions of gas and droplet and of the wall boundary layer were not solved in the analysis.

Oscillating unsteady flows are often encountered in supersonic-nozzle flows with condensation. The frequency range of the pressure fluctuations extends from about  $10^3$  to  $10^4$  Hz and the amplitude up to  $\pm 5\%$  of the mean value. These phenomena were studied theoretically and experimentally by Zierp and Lin (1968), Barschdorf and Fillipov (1970), Barschdorf (1967, 1971), Wegener and Cagliostro (1973) and Saltanov (1974). The cause is a feedback system caused by the movement of shock waves generated by the condensation. Such aspects can also be well predicted by the method of characteristics.

From these results it may be said that the features of nozzle flows with homogeneous nucleation and condensation can be predicted by one- or two-dimensional, inviscid gasdynamic theory coupled with a macroscopic nucleation-rate theory and a droplet growth law, provided that an empirical adjustment factor is found for the nucleation theory. In order to physically understand and predict the adjustment factor, further theoretical and experimental studies of the nucleation process are required on the basis of molecular dynamics for clusterization.

Applying the cluster kinetic theory of Buckle (1969) to condensation of water vapour in air, Pouring (1977) calculated the course of homogeneous condensation in a supersonic nozzle (see Section 2.4). It was shown that if a valid initial-equilibrium condition is well-established with the assumed

molecular parameters, the calculated nonequilibrium expansion closely matches the experimental pressure distribution. Although the estimation of the molecular parameters contains some uncertainties, this approach provides a kinetic aspect of the nucleation and condensation process.

Nozzle flows with heterogeneous condensation are often observed in chemical-engineering processes such as condensers, filters, and cooling towers. However, owing to the complications introduced by heterogeneous condensation, systematic fundamental studies of these flows as yet have not been done. Buckle and Pouring (1965) studied the effect of large numbers of smoke particles of silver iodide and other substances ( $0.1 \sim 1 \mu\text{m}$  diameters) artificially introduced in a supersonic nozzle and observed no difference in the wall pressure distributions with and without seeding. Wang (1976) investigated the effect of foreign nuclei on nitrogen condensation with a simple model that they provide only additional condensation surfaces. The result could not successfully explain the experiment showing low critical supersaturations. Saltanov and Tsirihin (1977) studied theoretically heterogeneous nucleation of nozzle flow and liquid-type nuclei. It is equivalent to homogeneous nucleation which has droplets of a specified size and concentration. Condensation of molecules occurs simultaneously on these nuclei and those nucleated homogeneously. It was shown that the addition of initial droplets by more than 0.1% of the concentration of nuclei nucleated homogeneously did not cause the pressure to deviate from their isentropic values.

For heterogeneous nucleation and condensation, the size-distribution of nucleus particles, the geometrical, physical and chemical characteristics of the nucleus surface and the electrical interaction between the nucleus particles and the gas mixture, take on important roles. These effects must be studied to ascertain the features of nozzle flows. At high droplet population densities, their coagulation due to Brownian-motion or turbulent-fluctuations will be appreciable. Wegener et al (1972) estimated that (within other uncertainties) coagulation could have little effect on the condensation process in a supersonic-nozzle flow of an ethanol-air mixture. However, since the coagulation process itself has unknown complicating factors, more quantitative studies of this effect are required.

Relative motions and relative differences of temperature between the condensate droplets and the gas mixture are usually assumed negligible (Wegener, 1969). Under some conditions with rapid changes in axial velocity and temperature, nonequilibrium flows result, where the thermal and kinematic parameters of the gas and the droplets differ. This leads to internal mass, momentum and energy fluxes between the constituents. The coupling of the two flow systems of vapour and droplets must be explicitly taken into account. Such studies have been carried out by Konorski (1976) for nozzle flows with slight deviations from the equilibrium state. Further extension of these studies to nucleation and condensation processes including particle coalescence would extend our knowledge of flow nucleation and condensation.

#### 4.3 Rarefaction and Expansion-Wave Flows

Nonstationary rarefaction-wave flows in the driver section of a shock tube or in a Ludwieg tube or steady expansion-wave flows around a sharp corner or in nozzles can result in vapour condensation, and offer additional techniques for the study of nucleation and condensation. Earlier work on these subjects up to 1974 was reviewed by Wegener (1975).



Steady-expansion flow around a sharp corner (a Prandtl-Meyer expansion, Fig. 10) provides cooling rates which decrease strongly away from the corner. The cooling rate varies from infinity at the corner to low values at large distances from the corner. Hence, for flows of condensing vapour, the features of nucleation and condensation depend appreciably on the radial distance from the corner. Since higher cooling rates result in higher supercooling at the onset of condensation, the onset supercooling decreases with distance from the corner. These phenomena were studied theoretically and experimentally by Steffen (1967), Tkalenko (1970), Smith (1971), Kurshakov et al (1971), and Frank (1977). Smith (1971) studied experimentally the expansion of moist air around a 40° sharp corner which was part of a lower block of a two-dimensional nozzle. A Mach-Zehnder interferometer was used to measure the density distribution. The result showed that the condensation zone was a strong function of both expansion angle  $\theta$  and radial distance  $r$  from the corner, as expected. The condensation front is curved (concave) to the oncoming flow and becomes parallel to the equilibrium characteristic behind the head of the expansion fan with increasing distance from the corner. The supercooling,  $T_s - T_c$ , where  $T_s$  is the saturation temperature and  $T_c$  the temperature at the onset of condensation, can be expressed as a function only of the local cooling rate ( $-\frac{dT}{dt}$ ):

$$T_s - T_c = 40.8 \left( -\frac{dT}{dt} \right)^{0.121} \quad (t: \mu\text{sec}) \quad (77)$$

for the range of  $1.7 > (-\frac{dT}{dt}) > 0.3 \text{ K}/\mu\text{sec}$ . Frank (1977) also investigated such flow fields of higher humidities ( $w_0 > 0.01$ ) and observed oblique shock waves within the expansion fan. At higher humidities, two clearly separated condensation zones were observed.

Barrand and Rieutord (1973) studied experimentally the nonstationary rarefaction-wave flow of water vapour-argon or helium mixtures in a long duct (8 cm dia x 201 cm long). The pressure history was measured at three points along the duct to detect the onset of condensation. With these results and other thermodynamic variables obtained from measurements of dry-gas expansions, they calculated a relation between cooling rate and supercooling at the onset of condensation which was approximately an extension of Smith's results (Fig. 11):

$$T_s - T_c = (1 \sim 2) \times 40.8 \left( -\frac{dT}{dt} \right)^{0.12} \quad (t: \mu\text{sec}) \quad (78)$$

for  $0.1 > (-\frac{dT}{dt}) > 0.02 \text{ K}/\mu\text{sec}$ .

In addition to cloud-chamber and nozzle-flow methods, the well-established shock-tube technique provides one more possibility for investigating experimentally and analytically nucleation and condensation processes. A shock tube in its simplest form consists of a straight constant-area duct which is divided by a removable diaphragm into a high-pressure driver section and a low-pressure driven section. By bursting the diaphragm, a shock wave rapidly develops and moves into the driven section, and an isentropic rarefaction wave propagates into the driver section (Fig. 12). Since the gasdynamic behaviour of such flows is now well-understood and easily controlled, rarefaction waves have proved most useful for investigating condensation. Other

applications of shock tubes to condensation studies were reported by Kung and Bauer (1971), Homer et al (1971), and Homer and Hurle (1972).

Rarefaction waves will suddenly expand isentropically mixtures of condensing vapour and noncondensable gas initially at rest in the driver section. The mixtures are cooled up to or below the supersaturation state. Further expansion leads to appreciable condensation of the vapour, which diminishes the supersaturation state. As the rarefaction-wave head moves into the mixture at rest in the driver with the state sound speed, the supersaturation along a particle path reaches a maximum and substantial cluster formation occurs. The onset of condensation can be observed by a sudden pressure rise with respect to the isentropic expansion and/or abrupt increase in the light scattering. Since in a flow with a higher cooling rate the onset of condensation occurs at a higher supercooling, the first onset in a shock tube takes place close to the tail of the rarefaction fan at a point close to the diaphragm where the cooling rate is high. Far from the diaphragm the onset moves toward the head of the rarefaction fan. Thus, the condensation-wave front has a curved path, as shown in the  $(x, t)$ -diagram or distance-time plane (Fig. 13). The heat released by condensation causes an appreciable change in the flow variables. Rarefaction waves within the driver section induce a subsonic flow behind them. The heat release changes the gasdynamic state along characteristics from the usual isentropic values downstream of the condensation zone, as shown by the bump in the  $(p, x)$  and  $(T, x)$  sketches at the "onset" (Fig. 13). Inside the condensation zone a two-phase flow of droplets and gas takes place, and under appropriate conditions, shock waves are produced (Sislian and Glass, 1976).

Actual rarefaction waves can be viewed effectively as a centred-wave system with a virtual origin not far from the actual diaphragm location. The virtual origin is determined by effects of fluid inertia for the initial acceleration, characteristics of diaphragm rupture and three-dimensional effects due to diaphragm curvature and associated shock-wave formation. Thus, close to the diaphragm, ideal simple centred waves are not realized. At large distances from the diaphragm, the ideality also deteriorates owing to the growth of wall boundary layers. Once the virtual origin is determined from measurements of static pressure the rarefaction fan in the intermediate distance range can be predicted from one-dimensional inviscid gasdynamics (Hall et al, 1974).

The shock-tube technique has the advantages of providing well-controlled experimental conditions which have the combined features of the cloud chamber and the supersonic nozzle. Like the cloud chamber, only small amounts of condensing substances are required, hence expensive or toxic species can be studied. It is also feasible to control vapour contamination by pumping to high vacuum prior to the experiments. As for supersonic-nozzle flow, shock-tube operation is well controlled and understood from one-dimensional inviscid gasdynamics, provided the initial pressures (Reynolds numbers) are not too low. The flow history along a particle path differs depending on its distance from the diaphragm. At different locations along the tube, a wide-range of cooling rates is obtainable from those of cloud chambers ( $10^{-2}$  K/ $\mu$ s) to those of supersonic nozzles (1 K/ $\mu$ s) (Table 1). Usually, the cooling rate is lower than in nozzle flows. However, contrary to cloud chamber and supersonic nozzle, the flow in shock tubes is nonstationary. During rapid expansion (near a corner or a diaphragm) nucleation takes place in a nonsteady process and the steady-state nucleation theory may not apply. However, for the range of usual cooling rates mentioned above, quasi-steady-state nucleation may be established in the available flow times.



Recently, Kawada and Mori (1973) successfully applied the rarefaction wave to study the nucleation and condensation rates of several refrigerant vapours by measuring the static pressure, density (Mach-Zehnder interferometer) and light transmission. The onset of condensation was defined as the point where the transmitted light was attenuated by 5%. The transmission efficiency of light is related to the size-distribution of droplets which can be predicted from nucleation and condensation rates. Thus, by measuring the onset time at a fixed location in the tube, the nucleation theory can be tested by experiments. They showed that the classical theory predicts well the experimental results with values of surface tension,  $\sigma/\sigma_\infty = 0.38$  for R-21, 0.69 for R-40, 0.61 for R-113 + argon, and  $\geq 1$  for  $\text{CH}_3\text{OH}$  + argon

Using rarefaction waves, Barschdorff (1975) also investigated the nucleation rate of water vapour in different inert gases (air, helium and argon) over a wide range of mixing ratios, and studied the carrier-gas effects on homogeneous nucleation of water vapour. The shock tube was evacuated to  $10^{-6}$  torr using a diffusion pump. Distilled, purified water vapour and a filtered, ultra-high-purity carrier gas (argon, helium or dry air) filled the driving chamber. The rarefaction process was studied by measuring the time histories of static pressure and light scattering. As in supersonic-nozzle flows, the mass fraction of condensate  $g$  was computed by integrating Eq. (55) along a particle path with a macroscopic nucleation theory, Eq. (74). When the onset of condensation is of primary interest, the gasdynamic state of flow can be greatly simplified by adjusting the initial diaphragm pressure ratio so as to make the onset coincide with the tail of the rarefaction wave at the observation point. Then, there is no influence of prior condensation in the rarefaction fan and an isentropic state is preserved up to the onset (Wu, 1977). The value of  $\Gamma$  in Eq. (74) was chosen for which the strong increase in nucleation rate matched well with the observed onset of condensation. The results show a variation of  $10^6 \leq \Gamma \leq 1$  between the limits of low vapour concentration ( $\omega_0 = 0.003$ ) to pure steam ( $\omega_0 = 1$ ). No systematic deviations due to the type of carrier gas were observed. The calculation of  $\Gamma$  was performed by using the surface tension corresponding to the bulk value  $\sigma_\infty$  and the condensation coefficient of unity in the droplet growth. Although this assumption may explain partially the large deviation of the  $\Gamma$  values, further theoretical work is necessary for its understanding on a basis of two-component, two-phase statistical mechanics or kinetics.

Lee (1977, 1978) employed the same method for evaluating his experiments on condensation of water, heavy water ( $\text{D}_2\text{O}$ ), benzene ( $\text{C}_6\text{H}_6$ ), carbon tetrachloride ( $\text{CCl}_4$ ), and freon 11 ( $\text{CCl}_3\text{F}$ ) in argon. No difference was observed in the condensation of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The values of  $\Gamma$  calculated were  $10^3 \sim 10^5$  for  $\text{H}_2\text{O}$ ,  $10^1 \sim 10^3$  for  $\text{D}_2\text{O}$  and  $\text{C}_6\text{H}_6$ ,  $10^2 \sim 10^4$  for  $\text{CCl}_4$ , and  $10^9 \sim 10^{12}$  for freon 11.

Kalra (1975) and Glass et al (1977) investigated the condensation of water vapour in a nitrogen carrier gas. The time variations of density gradient and static pressure as well as the onset of condensation were monitored at two fixed locations in the driver section by using a laser Fabry-Perot interferometer, a differential interferometer and piezotron transducers. The effects of the cooling rate on the supersaturation at the onset of condensation provided an empirical relation:

$$\frac{T_s - T_c}{T_s} = 1.73 \times 10^{-3} \left( -\frac{dT}{dt} \right)^{0.39} \quad (79)$$

for  $0.09 > (-dT/dt) > 0.04 \mu\text{sec}$ . This result coincides approximately with those of Smith (Eq. 77), and Barrand and Rieutord (Eq. 78), as seen in Fig. 11.

Several analyses of rarefaction-wave flow of a mixture of water vapour and nitrogen in a shock tube were done by Sislian (1975), Sislian and Glass (1976), Kotake and Glass (1976, 1977), Glass, Kalra and Sislian (1977) and Glass and Sislian (1977). The method of characteristics and the Lax method were used along with a macroscopic nucleation theory. To construct a mathematical formulation of one-dimensional nonstationary flow in a shock tube, the same assumptions were employed as for nozzle flows: an inviscid, nonconducting perfect gas mixture, no-slip velocity condition, identical temperatures of condensate and gas mixture, and a uniform distribution of the condensate across the tube section. The governing equations are:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} = 0$$

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = -\frac{1}{\rho} \frac{\partial p}{\partial x} \quad (80)$$

$$\frac{dh}{dt} = \frac{1}{\rho} \frac{dp}{dt}$$

with  $t$  - time, and  $x$  - distance from the diaphragm along the shock tube. The equation of state is given by

$$p = \left( \frac{1 - \omega_o - g_p}{\mu_g} + \frac{\omega_o - g}{\mu_v} \right) \rho RT$$

and the specific enthalpy is

$$h = c_{p0} T - Lg$$

where

$$c_{p0} = (1 - \omega_o - g_p) c_{pg} + \omega_o c_{pv} + g_p \frac{h_p}{T}$$

The production of the condensate mass along a particle path can be expressed by Eq. (56) or Eq. (63) in which the nucleation rate and the droplet-growth rate are given by Eqs. (18) or (39) and (47), respectively.

The above set of equations were solved numerically using a second order characteristic method subject to the initial conditions. Sislian (1975) and Sislian and Glass (1976) calculated the case of homogeneous condensation for water vapour-nitrogen mixture of  $\omega_o = 0.01776$  and  $T_o = 295.3 \text{ K}$  (Figs. 13, 14 and 15). As shown in Fig. 13, the characteristics emanating from the



origin remain straight as long as the effect of homogeneous condensation on the flow variable is negligibly small. After penetrating the condensation zone the characteristics begin to curve appreciably towards the head of the rarefaction wave due to the heat release from condensation. Computations showed that, for the case considered, the condensation wave is followed by a shock wave generated by the intersection of characteristics of the same family. The width of the condensation wave (zone) increases with increasing distance from the origin due to the interplay of two varying opposing effects of decreasing pressure due to expansion and increasing pressure due to the heat release from condensation. Close to the origin where the expansion rate is very high, appreciable condensation takes some time to occur. However, in this region, the steady-state nucleation theory may not be applicable in order to obtain detailed flow information.

The presence of shock waves in the flow field complicates the numerical solution of the problem. In order to handle such discontinuities, Lax's method of implicit artificial viscosity is used. This technique requires that the governing equations be expressed in Lagrangian form:

$$\begin{aligned}\frac{\partial}{\partial t} \left( \frac{\rho_0}{\rho} \right) &= \frac{\partial u}{\partial \xi} \\ \frac{\partial u}{\partial t} - \frac{1}{\rho_0} \frac{\partial p}{\partial \xi} &= 0 \\ \frac{\partial e}{\partial t} + \frac{p}{\rho_0} \frac{\partial u}{\partial \xi} &= 0\end{aligned}\tag{81}$$

with  $\xi$  - Lagrangian parameter which identifies a fluid element, taken as the spatial coordinate at the time origin  $t = 0$ ;  $\rho_0$  - density of the fluid element  $\xi$  at  $t = 0$ . The agreement between both calculations was satisfactory except in the region close to the origin. The analyses were compared with the experiments of Karla (1975) and Glass et al (1977) (Fig. 15). The pressure history shows a significant discrepancy between analysis and experiment. If the value of the macroscopic surface tension ( $\sigma_\infty = 82$  dyne/cm) is adjusted to a lower value ( $\sigma = 68$  dyne/cm),  $\sigma/\sigma_\infty = 0.83$ , the analysis can be made to match the experimental data fairly well except for the value of supersaturation at the onset of condensation.

Kotake and Glass (1976, 1977) studied an alternative heterogeneous condensation analysis. Fine condensation nuclei of solid particles (Aitken nuclei) with radii below  $0.1 \mu\text{m}$  were assumed to exist after usual filtrations (Mason, 1971, Boucher, 1969). A size distribution of nuclei was assumed

$$\frac{dN}{d \ln R} = 10^5 \left( \frac{R}{R_0} \right)^{0.25} \exp \left\{ - \left( \frac{R}{R_0} \right)^{1.5} \right\}\tag{82}$$

where  $R_0 = (1.5 \sim 5) \times 10^{-6}$  cm (Fig. 16). All particles were assumed to have a smooth, spherical shape of effective radius without any coagulation or separation which were chemically inert and insoluble in water vapour. Rarefaction wave flows with heterogeneous condensation were numerically calculated

using macroscopic heterogeneous-nucleation theory, Eq. (39), and condensate-mass equation, Eq. (63), coupled with the flow equations. Owing to the complexity and variety of collisions between monomers and the solid surface of nuclei, it is difficult to estimate the values of the vibrational frequencies of atoms, the desorption free-energy of monomers and the contact angle. Fortunately, the first two factors are not significant compared with the contact angle. The computations showed that the features of heterogeneous condensation are dominated largely by the contact angle.

The contact angle directly affects the activation energy. The value  $\theta = 180^\circ$  implies the same value of activation energy as homogeneous nucleation, whereas  $\theta = 90^\circ$  yields a value reduced by about 50%. Less activation energy results in a higher nucleation rate with lower supersaturation, lower supercooling, a higher propagation velocity of the condensation wave and a narrower condensation zone. The calculated results show these patterns by comparison with the homogeneous case. By choosing a suitable value for the contact angle ( $\theta \approx 90^\circ$ ), the experimental data could be fitted fairly well, again except for the supersaturation at the onset of condensation (Fig. 15).

By using macroscopic models of homogeneous and heterogeneous nucleation with a suitable value of the surface tension and the average contact angle, respectively, condensation in rarefaction waves in a shock tube can be predicted. Although the experimental results can be explained equally well by either homogeneous or heterogeneous-nucleation theory, many factors remain unsolved such as coagulation, solubility and electrical charges. Nevertheless, the procedure of choosing values of surface tension or contact angle to fit experimental data is not a satisfactory one. At best they are a guide for decisive quantitative measurements of these parameters under actual conditions.

The vapours treated above can be condensed to the liquid phase only by expansion. However, the so-called "retrograde" fluids can change their phase from vapour to liquid by "compression". In the phase change, these fluids store the latent heat in the condensate state within a large number of internal (vibrational) molecular degrees of freedom. This is the case if the heat capacity of a fluid at a reference state is sufficiently large. All the fluids in the paraffin family, say hydrocarbon series above the complexity level of propane, n-hexane or n-octane, show this retrograde behaviour and under some conditions condensation from the vapour phase to the liquid phase will be produced by a shock wave.

Thompson and Sullivan (1975) studied the possibility of such "liquefaction" shock waves. They showed that for fluids which have an ideal gas specific heat  $\alpha_v > 24 R$  at the critical temperature, "complete condensation or liquefaction shocks" can be found in relatively simple experiments. A "complete condensation shock" means that the upstream state is "fully dry" and the downstream state is "fully wet". Dettleff, Thompson and Meier (1976) and Dettleff et al (1976) carried out experimental studies of condensation induced by liquefaction shocks using a shock tube with various fluorinated hydrocarbons as the test fluid. Measurements of pressure, shock velocity and temperature showed good agreement with the Rankine-Hugoniot relations, and a clear liquid-phase condensate was photographically observed behind the shock front. Although further studies are required for a quantitative description of the flow field, this new aspect of condensation will provide additional approaches to the development of nucleation and condensation theories.



#### 4.4 Free-Molecular Jets

Most experiments on nucleation and condensation of vapour were limited to examining the supersaturation at which appreciable condensation occurs. Only information integrated over many complex intermediate steps is available. Consequently, the details of the collision kinetics are hidden. A quantitative interpretation of each step, from monomer or dimer collisions to droplet formation, is difficult to obtain from macroscopic measurements such as droplet size, pressure, density or temperature. To provide all the desired information on nucleation, an ideal experiment would make it possible to observe each stepwise event. Molecular-beam sampling of a free jet seems capable of providing such information. For this reason, it has been used intensively during the past decade for the study of nucleation kinetics of early clustering stages.

A free-jet expansion consists of allowing a gas in collision-dominated continuum flow to expand through an orifice or nozzle into a region which is maintained at high vacuum (Fig. 17). As the gas expands from the source into a vacuum, random thermal motion is converted to directed motion and the gas is accelerated to sonic flow at the nozzle throat. Beyond this, the gas near the centre of the jet expands supersonically as a nearly-isentropic continuum flow until it becomes rarefied enough to become a free-molecular flow. Typical pressures drop three to four orders of magnitude and temperatures fall to a few degrees Kelvin. The rate of expansion is controlled by the orifice or nozzle diameter, since the expansion history of the gas is scaled with distance (in diameters) downstream of the sonic throat. As shown schematically in Fig. 16, the core of this low-density jet is then usually skimmed into a molecular beam through a small hole at the tip of a conical "skimmer" located downstream of the nozzle. Usually, continuum flow exists upstream of the skimmer and free-molecular flow downstream. Under many conditions, a transition from continuum flow to free-molecular flow occurs upstream of the skimmer. Molecules flying near the system centreline are then passed through a collimating orifice into a detection chamber.

During the initial high-density stage of the expansion, the precipitous adiabatic decrease of temperature relative to pressure may initiate homogeneous nucleation if the gas becomes supersaturated and the growth of molecular clusters can occur until the collision rate decreases for molecular flow (Fig. 18). If the sampling process is carried out without materially disturbing the flow, one can obtain a so-called condensed molecular beam, i.e., cluster beams in arbitrary stages of condensation arising from upstream stagnation conditions. They are made up of clusters, i.e., microdroplets or microcrystals where atoms or molecules are held together by Van der Waals forces. Clusters are viewed as species with properties which are intermediate between those of homogeneous monomolecular vapour and those of bulk condensate. Determination of the beam composition can be conveniently carried out by gas-scattering methods, light-scattering methods, electric or magnetic mass spectrometers, retarding mass spectrometers, time-of-flight mass spectrometers and electron-beam diffraction methods.

Figure 18 shows the increase in Mach number  $M$  with distance  $x/d$  from the throat to its design value, the rapid drop in temperature  $T$  and the increase in concentration of the condensate clusters  $n_2, n_3, \dots$ . The kinetic process of clustering produces clusters of smaller size at higher rates ( $n_2 > n_3 > \dots$ ) of which concentrations are considerably lower than the equilibrium values corresponding to the temperature.

In the last decade, the study of dimer and cluster formation in supersonic free jets has been advanced by many investigators, such as: Milne and Greene (1967, E), Milne, Vandegrift and Greene (1970, A), Golomb, Good and Brown (1970, E, A), Gordon, Lee and Herschbach (1971, E, A), Golomb et al (1972, E), Hagena and Obert (1972, E), Dittmers, Schütze, Fischer and Schügerl (1972, E), Yealland, Deckers, Scott and Tuori (1972, E), Stein and Armstrong (1973, E), Sinha, Schultz and Zare (1973, E), Dorfelf and Hudson (1973a, b, A), Van Deursen and Reuss (1973, E), Good and Golomb (1974, E, A), Hagena and Wedel (1974, E), Armstrong and Stein (1974, E), Seary and Fenn (1974, E), Beylich and Robben (1974, E, A), Seary (1975, A), Calo (1975, E, A), Beylich (1976, E, A), Van Deursen and Reuss (1977, E), Van Deursen and Reuss (1977, E), Knuth (1977, A), where E and A denote experimental and analytical studies, respectively.

In Table 3 the experimental studies are listed, showing the investigator, species of cluster, diameter of nozzle or orifice (d), range of source pressure ( $p_0$ ) and temperature ( $T_0$ ), type of detector, and the main results. For gases such as Ar, Kr, Ne, Xe,  $N_2$ ,  $O_2$ , NO, CO,  $SO_2$ ,  $CO_2$ , K, Rb, Cs, Na and  $H_2O$ , cluster concentrations and cluster sizes have been measured mass-spectrometrically as a function of source pressure, temperature, and nozzle diameter. Figure 19 shows typical total and individual mass beam intensities against source pressure. As the source pressure is increased with keeping the source temperature constant, the total-beam intensity increases slowly to a plateau due to the larger number of collisions resulting from the longer continuum expansion and the initial state closer to saturation. After the plateau, it follows a slow decrease and then a steep increase. The decrease after plateau is attributed to skimmer interaction. The steep increase is due to heavier clusterization, being associated with decreasing monomer intensity and increasing dimer and cluster intensities. After reaching a maximum, the dimer and cluster intensities decline and indicate condensation or coalescence of clusters into droplets which are not detected by the mass spectrometer. Thus, the peaks of dimer or cluster curves can be related to the condensation process. The position of the peaks depends on the expansion history, that is, the source pressure  $p_0$ , temperature  $T_0$  and the nozzle or orifice diameter (d) in the form  $d p_0 T_0^{-n} = \text{constant}$ .

For correlation of the onset of cluster condensation, the following relations have been obtained experimentally or analytically by several investigators:

$$d^{0.55} p_0 T_0^{-2.2} = \text{const.} \quad \text{for Ar, Golomb et al (1970)}$$

$$d^{0.6} p_0 T_0^{-2.2} = \text{const.} \quad \text{for Ar, Kr, } CO_2, SO_2, N_2, CO \text{ and NO,}$$

Good and Golomb (1974)

$$d^{0.8} p_0 T_0^{-2.4} = \text{const.} \quad \text{for Ne, Ar, Kr, Xe, } N_2 \text{ and } CO_2,$$

Hagena and Obert (1972)

$$d^{0.55} p_0 T_0^{-2.25} = \text{const.} \quad \text{for Ar, Ne, } H_2, N_2 \text{ and } O_2,$$

Van Deursen and Reuss (1977)



A more detailed knowledge of how gas properties and the source conditions including nozzle geometry affect cluster formation can be obtained by considering similarity conditions of the phenomena. Such similarity relationships have been developed by Hagena (1969, 1974), Hagena and Obert (1972) and Good and Golomb (1974).

Fundamentally, the process of cluster formation may be solved by using the appropriate kinetic equations of clusterization. The propriety of the kinetics can be confirmed by comparing the results with experiments. In order to arrive at meaningful results, a substantial knowledge is required of free-jet expansion from continuum flow to free-molecular flow. However, a complete description of such flow fields including the subsonic region has never been given for a small orifice or nozzle. It is not possible at present to give a complete history of the states to which the clusters may be exposed. During the very first stage of the expansion, the state of the system changes slowly enough that equilibrium is maintained. As the expansion proceeds, the time scale for change in the clustering environment becomes so small that equilibrium cannot be maintained. Departure from equilibrium occurs as soon as the flow leaves the nozzle. Experimentally and analytically, it is shown that the expansion of chemically inert gases remains isentropic up to a so-called "terminal Mach number" which can be calculated from the gas properties and the orifice or nozzle size. In this range, using numerical methods, the state of the gas in a free jet can be computed for a given orifice or nozzle and the stagnation conditions. Calculations of such flows have been carried out for various specific-heat ratios, and algebraic fitting relations are available which provide a close approximation to the numerical results. Further expansion quickly brings about a transition to free-molecular flow. For the transition process from continuum to free-molecular flow, a number of studies have been done in the last decade by using methods such as the sudden-freeze model, simple kinetic theory, BGK-model and Monte Carlo methods. For large Mach numbers ( $M > 3$ ) and large nozzle Reynolds numbers ( $Re > 200$ ), the gas remains in thermodynamic equilibrium up to the terminal Mach number. Thereafter, its axial translational-energy distribution and the parallel temperature remain "frozen" at the terminal Mach-number value.

Application of the above flow features to the clustering process in a free-jet expansion makes it feasible to analyze the kinetic process of cluster formation without introducing troublesome and detailed flow structures. For one-dimensional isentropic expansion with negligible effects from molecular transports, thermal radiation and external fields, the equations of mass, momentum and energy give

$$\begin{aligned} \frac{d}{dx} (\rho u A_f) &= 0 \\ \rho u \frac{du}{dx} + \frac{dp}{dx} &= 0 \\ \frac{d}{dx} \left( h + \frac{1}{2} u^2 \right) &= 0 \end{aligned} \quad (83)$$

where  $\rho$  is the density of the gas and cluster mixture,  $u$  the axial velocity,  $p$  the pressure and  $h$  the enthalpy. Although the cross-sectional area of the

flow  $A_f$  is an important variable and is not available without solving the two-dimensional problem, the result for a free-jet expansion of chemically inert gases can be used approximately. The equation of state is

$$p = \rho RT \quad (84)$$

where  $R$  is the gas constant of the mixture. The rate equation of cluster formation can be written as

$$u \frac{dn_i}{dx} = q_i(n_1, n_2, \dots, n_N, p, T) \quad (85)$$

where  $n_i$  is the concentration of  $i$ -mer. Generally, the enthalpy is expressed as the sum of  $i$ -mer enthalpies

$$h = \sum_i \frac{n_i}{n_o} (h_{\text{trans}}^i + h_{\text{rot}}^i + h_{\text{vib}}^i + \Delta h^i)$$

where  $h_{\text{trans}}$ ,  $h_{\text{rot}}$  and  $h_{\text{vib}}$  denote enthalpy contribution due to  $i$ -mer translational, rotational and vibrational motion,  $\Delta h^i$  the  $i$ -mer formation energy and

$$n_o = \sum_{i=1} n_i \quad (86)$$

When the rotational and vibrational-relaxation process of clusters must be taken into account, an appropriate mechanism must be assumed.

For small fractions of clusters, the enthalpy, density and gas constant can be approximated with those of chemically inert gases, and the temperature and velocity distributions along the flow axis which are obtained for inert gases can also be utilized. Thus, Eqs. (83) to (86) are easily solved. With this method, dimerization in free jets was calculated by Milne et al (1970) for Ar, Golomb et al (1970) for Ar and NO, Gordon et al (1971) for K, Rb and Cs, Dorfled and Hudson (1973) for CO<sub>2</sub>, Beylich and Robben (1974) for Ar, Seary (1975) for H<sup>+</sup>H<sub>2</sub>O, Calo (1975) for H<sub>2</sub>O, Beylich (1976) for N<sub>2</sub>, and Knuth (1977) for Kr, Ar and Ne (Table 4).

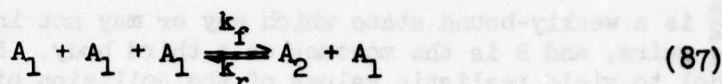
As for the kinetic process, it is difficult to establish a quantitative scheme without prior knowledge of the rates of the clustering processes. In the first stage of expansion, the cluster kinetics is primarily governed by a single cluster species. Once conditions in the jet favour the growth of this species, formation of large clusters will occur without a significant rate of cluster dissociation. The size of the rate-controlling cluster may be a function of the expansion history. For fast, low-density expansions, the size will be small, and the cluster will consist largely of dimers.

As for dimer formation from the vapour, two processes may be considered from kinetic theory; a termolecular mechanism of three-body



collision with dimer destruction by bimolecular collision, and a stabilization mechanism of intermediate dimer-complexes (see Table 4) in a virtual-orbiting state or of quasibounded states. It is well known that two-body collision of hard spheres can lead to bound dimers only in exceptional cases. Dissociation of dimers will occur through collisions with monomers. Other factors such as trimer formation and dissociation will be assumed to have a negligible effect on the initial kinetics. The major influence occurs solely through dimer-monomer interactions. For this process kinetic equations can be developed in a straightforward manner from collision theory.

A termolecular mechanism of dimer formation



is employed by Milne et al (1970) for Ar, Golomb et al (1970) for Ar and NO, Gordon et al (1971) for K, Rb and Cs, Dorfeld and Hudson (1973) for CO<sub>2</sub>, and Calo (1975) for H<sub>2</sub>O. The forward rate constant  $k_f$  may be taken as the normal termolecular collision rate constant. From kinetic theory,

$$k_f = 8\pi^{3/2} \beta l_3^4 \left( \frac{kT}{m} \right)^{1/2} \quad (88)$$

with  $\delta$  - two-body collision diameter,  $l_3$  - approach distance of the three molecules ( $\approx \delta$ ) and  $\beta$  - collision effectiveness written as  $\beta = \beta_0 \exp(-\epsilon/kT)$ . Although internal degrees of freedom of the dimer are not always equilibrated, for a first-approximation treatment the reverse reaction constant may be related to the forward reaction rate through the equilibrium constant  $K_e$ , on the assumption of microscopic reversibility. The rate of dimer formation is then

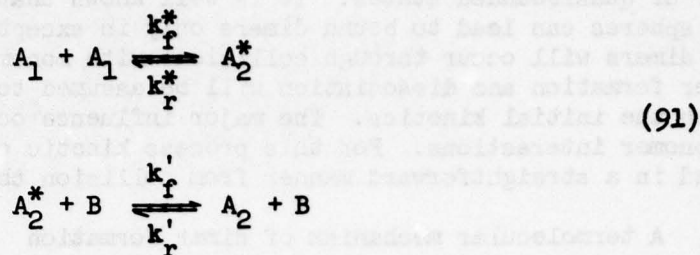
$$u \frac{dn_2}{dx} = k_f \left( n_1^3 - \frac{1}{K_e} n_1 n_2 \right) \quad (89)$$

Golomb et al (1970) predicted dimer concentrations with  $\beta = 1$  and  $l_3 \approx \delta$ . The predicted values were lower than their measured values. Milne et al (1970) also calculated argon dimer concentrations and looked for a temperature-dependent rate coefficient to predict their measured values. They found that  $k_f$  proportional to either  $T^{-2}$  or  $T^{-3}$  could most nearly reproduce the experimental data. Fordon et al (1971) calculated alkalidimer concentrations taking into account vibrational relaxation and heat of condensation to compare their experimental data, adjusting the collision diameter and the extent of vibrational relaxation. They found that the collision cross-section was 3.6 times the hard-sphere value and roughly half or more of the heat of condensation converted to vibrational excitation of the dimer molecules. Calo (1975) considered water dimer formation, using the collision diameter

$$\delta = \delta_0 \left( 1.665 \frac{T}{T_\epsilon} \right)^{0.283} \quad (90)$$

where  $\delta_0 = 2.71 \text{ \AA}$  and  $T_\epsilon = 506 \text{ K}$ . The calculated results were in good agreement with the experimental data.

In the stabilization of intermediate complexes, the dimer formation occurs in two steps,



where  $A_2^*$  is a weakly-bound state which may or may not include metastable and orbiting pairs, and B is the monomer or a third body. Knuth (1977) employed this model to yield realistic values of the collision effectiveness for dimer formation of rare gases. He assumed that the gas is in local thermodynamic equilibrium from the source to a sudden-freeze surface the location of which is a function of the local reaction-rate coefficient. The relaxation process, that is, the mole fraction of dimers frozen downstream of the surface. The location of the sudden-freeze surface was given by

$$u \frac{d\tau_{h.p}}{dx} = \frac{1}{2} \quad (92)$$

where  $\tau_{h.p}$  is the relaxation time for the reaction of dimer formation at constant enthalpy and pressure, and is inversely proportional to the reaction-rate constant. A quantitative relation between the terminal dimer-mole fraction, source conditions and the local recombination coefficient  $k_f$  was obtained. From the experimental data for Kr, Ar and Ne, the collision effectiveness was estimated as

$$\beta = 0.4 \exp \left( - 0.6 \frac{\epsilon}{kT} \right) \quad (93)$$

and the terminal mole fraction of dimers was expressed approximately as

$$\frac{n_2}{n_1} \approx 0.5 \left\{ n_0 \delta^3 \cdot \left( \frac{\epsilon}{kT_0} \right)^{7/5} \cdot \left( \frac{d}{\delta} \right)^{2/5} \right\}^{5/3} \quad (94)$$

where  $n_0$  is the source number density.

Although the dimer formation in free-jet expansions can be predicted by the theoretical treatments mentioned above using the flow features of inert gases, the relevant collision-kinetics problems still remain to be solved. In this regard, Beylich (1974) studied the argon dimerization by using a Lennard-Jones interaction potential and a kinetic model to describe the mass fluxes between the vibrational states of the dimer and the atom including the effect of the flow field and tunneling, as well as the association due to binary collision. However, further studies in this direction are required for more complex substances as well as complex systems such as binary mixtures and heterogeneous mixtures.



As for larger clusters than dimers, the kinetics are readily developed with bimolecular-collision theory between monomer and i-mers, Eq. (2),

$$u \frac{dn_i}{dx} = (c_{i-1}n_{i-1} - e_i n_i) - (c_i n_i - e_{i+1} n_{i+1}) \quad (i \geq 3) \quad (95)$$

For given pre-expansion conditions, it may be assumed that the clustering kinetics are mainly governed by a single cluster species. Since the monomer cannot serve as the rate-controlling species for a termolecular collision, the smallest possible rate-controlling cluster is a dimer. Once conditions favour conversion of dimers to trimers, the formation of larger clusters will occur. Dorfeld and Hudson (1973b) developed such a kinetic analysis for CO<sub>2</sub> clusters. In an expansion from room temperature, most nonpolar gases such as CO<sub>2</sub> exhibit a minimum in equilibrium-cluster mole-fraction. The clustering process was assumed to initiate at the point where the equilibrium trimer mole-fraction becomes equal to the dimer mole-fraction. Dimer concentrations were predicted from the kinetic equation of dimerization with negligible depletion through trimer formation. The observed cluster populations were explained well by the theory.

Beylich and Robben (1974) also studied the cluster formation of larger numbers of argon atoms (> 50). They measured the distributions by means of a time-of-flight mass spectrometer, and compared them with numerical calculations. The cluster growth was adequately described by kinetic theory, whereas classical steady-state theory could not predict the onset of condensation and the cluster distribution. Beylich (1976) also compared the theoretical results with experiments of condensation in a nitrogen free-jet expansion. The calculations showed that classical quasi-equilibrium nucleation rates could yield comparable results only if an additional term in the free energy of about 7 kT was added. Also, the kinetic method of Pouring (1977) and Kanyukhov and Faizulaev (1977), as well as the molecular dynamics method of Zurek and Schieve (1978) can be extended to clusterization in free-molecular jets with sufficient consideration of the relevant parameters.

Another situation of practical interest concerning free-molecular jets is the problem of the exhaust of rocket gases into space. Recently Wu (1975) examined the possibility of nucleation and condensation of certain species in the exhaust plume of an Apollo rocket engine at high altitudes. Assuming steady macroscopic nucleation theory with the nonisothermal correction (Eq. 74) and using empirical results for the plume flow field, the accumulation of condensate was calculated. The result showed an expectation of water-vapour condensation in the plume downstream of the nozzle, although the nonsteady process of clusterization could delay the onset of condensation. For relevant problems, further work will be required for nonsteady, homogeneous and/or heterogeneous nucleation and condensation in continuum and free-molecular flows.

## 5. CONCLUDING REMARKS

A review has been given of recent studies of homogeneous and heterogeneous nucleation and condensation and some of their associated steady and nonstationary flows. For most experiments in cloud chambers, supersonic

nozzles and shock tubes, homogeneous nucleation and condensation are well-described by the so-called classical theory of the quasi-steady macroscopic drop model or its modified theory with a correction factor. Although the factor varies in the range from 1 to about  $10^{20}$ , once such a correction is made empirically, nucleation and condensation for most of these technical problems can be predicted with sufficient reliability by the gasdynamics of diabatic flows with phase transitions. Here the condensate can be assumed as finely dispersed with a no-slip velocity from the gas phase. Nucleation and condensation are noted primarily for the effects from the heat release of the latent heat of vapourization. The correction factor for the nucleation theory of the macroscopic-drop model stems from a fundamental lack of knowledge of the volume and surface free-energy of small clusters and the Brownian motion of the cluster. Thus, knowledge of the actual values of  $\sigma$  (surface tension),  $\alpha_c$  (condensation coefficient) and  $\Gamma$  (correction factor) remains to be uncovered before condensation flow can be predicted analytically with confidence.

Contrary to the expansion cloud-chamber, the diffusion cloud-chamber produces a steady diffusing stream with a temperature gradient. The stationary conditions in the chamber can be calculated using one-dimensional heat and mass diffusion relations. Nucleation in ordinary diffusion chambers is predicted well using the classical theory of the drop model. By employing supersonic nozzles or rarefaction waves in a shock tube, nearly-stationary or nonstationary two- or one-dimensional inviscid flows can be obtained where the expansion rate is not large enough to produce nonsteady nucleation effects. The observed static pressure distribution or history of the flow along the nozzle or tube axis agrees well with the one-dimensional, inviscid mass, momentum and energy flow equations coupled with a growth-rate equation for the condensate and a nucleation rate for the macroscopic-drop model with a suitable correction factor. Alternatively, a fit of the numerical calculations to the observed results provides a test for the nucleation theories. An estimation can also be made of uncertain properties such as the correction factor, the condensation coefficient, and the macroscopic surface-tension.

In general, the experimental results for a given substance using a cloud chamber are found to be in agreement with the results from supersonic-nozzle and shock-tube flows. However, the magnitude of the correction factor varies over a very wide range as noted above. Thus, when a correction is used in conjunction with the drop model, the behaviour of the nucleation process must be known a priori so as to be able to estimate the correction factor. In order to predict such uncertain properties as well as to establish a nucleation theory for small clusters, two major approaches, quasi-steady and nonsteady, have been developed. The first is a statistical-mechanical approach (quasi-steady) focusing attention on the partition functions of clusters and the size distribution of clusters in an association-dissociation equilibrium state. The second is a kinetic approach (nonsteady) from molecular dynamics of cluster formation.

With the aid of large high-speed computers, the evaluation of thermodynamic properties of clusters over a wide range of size and temperature becomes feasible using molecular-dynamic or Monte Carlo techniques. Although it requires a detailed knowledge of molecular or atomic interactions (potentials), the study is in gradual progress from simple cluster systems such as argon vapour to more complex systems, e.g., water vapour. However, it is unlikely that in the near future sufficiently realistic intermolecular potentials will be developed



for complex-cluster systems. The assumed intermolecular potentials must be tested and verified by comparing the calculated thermal properties with experiments. In turn, it means that more detailed experiments are required for an understanding of the features of small clusters. The ideal experiment for such a study would be one in which the process of clusterization could be frozen at an arbitrary size or stage. This would provide detailed information on clusterization kinetics. One of the most promising methods for this purpose is the free-molecular-jet technique coupled with mass spectrometry. In this system, the effects of thermal nonequilibrium and relaxation time are extremely important, and a detailed treatment of the kinetics is necessary. The kinetics of clusterization can be described by molecular-collision kinetics. Experimental results from free-molecular-beam methods provide tests for the kinetic model of cluster formation. However, only rather simple processes of clusterization such as dimerization have been studied to date. In this manner a gradually-growing knowledge of cluster formation will lead to a better understanding of small clusters as well as the nucleation process in free-molecule flows such as venting-vapour flows of spacecraft, rocket exhausts at high altitude, and condensed-matter formation in astrophysical problems.

Most nucleation and condensation studies have been concerned with homogeneous processes owing to the simpler modelling aspects required for a theoretical understanding. Nucleation of molecules on ions and other impurities is of considerable importance in actual and practical problems such as the formation of clouds and aerosols, metallurgical condensation on substrates, clusterization of excited species in combustion, and condensation trails of rocket exhausts. There exist many similarities between homogeneous and heterogeneous-nucleation processes. Current theories of heterogeneous nucleation are mainly centred around macroscopic concepts, being essentially extensions of homogeneous-nucleation theories. These theories can explain macroscopic features of the observed phenomena. However, as in the homogeneous case, ultimately a theoretical explanation must be phrased in molecular terms. In this regard, it can be expected that the free-molecular-beam technique will provide a promising path towards understanding the heterogeneous nucleation processes.

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Table 1 - Cooling Rates Obtainable in Various Flows

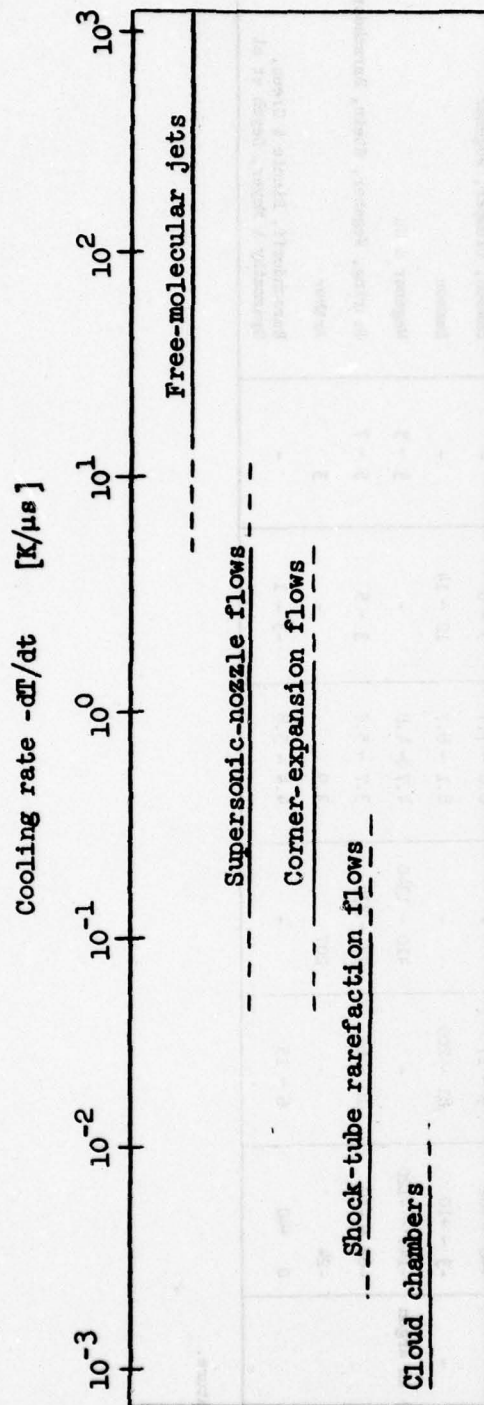


Table 2 - Comparison of Homogeneous Nucleation Results in Supersonic-Nozzle and Shock-Tube Flows with Classical Theory  
(Wegener & Wu, 1977)

| Substances                                   | $T_c - T_{mp}$<br>K | $T_c - T_{mp}$<br>(1) | Supersaturation s |            | Critical<br>Radius $r^*$ , Å | Correction Factor $\log_{10} f$ |       | Investigators  |
|--|---------------------|-----------------------|-------------------|------------|------------------------------|---------------------------------|-------|--|
|  |                     |                       | Liquid            | Solid      |                              | Liquid                          | Solid |  |
| Ammonia ( $NH_3$ ) in air                    | +2                  |                       | 4                 | -          | 8.7                          | 12                              | -     | Jaeger   |
| Benzene ( $C_6H_6$ ) in air                  | -78 ~ -63           |                       | 59 ~ 158          | 175 ~ 700  | 7.8 ~ 8.0                    | 8 ~ 9                           | 2 ~ 4 | Dawson   |
| Carbon tetrachloride ( $CCl_4$ )<br>in argon | -50 ~ -30           |                       | 4 ~ 8             | -          | 9.0 ~ 9.6                    | 6 ~ 7                           | -     | Barschdorff  |
| Chloroform ( $CHCl_3$ ) in air               | -3 ~ +24            |                       | 8 ~ 25            | -          | 9.4 ~ 13.0                   | 11 ~ 22                         | -     | Dawson, Barschdorff  |
| Ethanol ( $C_2H_5OH$ ) in air                | +48 ~ +62           |                       | 9 ~ 17            | -          | 6.8 ~ 7.7                    | 5 ~ 6                           | -     | Dawson, Clumper, Wegener                                       |
| Freon 11 ( $CCl_3F$ ) in air                 | -3 ~ +10            |                       | 81 ~ 200          | -          | 8.1 ~ 8.7                    | 12 ~ 14                         | -     | Dawson   |
| Sulphur hexafluoride ( $SF_6$ ) in argon     | -144 ~ -120         |                       | -                 | 410 ~ 1340 | 4.7 ~ 4.8                    | -                               | 3 ~ 5 | Wegener & Wu   |
| Water ( $H_2O$ ) in air                      | -62 ~ -19           |                       | 10 ~ 67           | 77 ~ 334   | 3.7 ~ 5.7                    | 3 ~ 5                           | 5 ~ 7 | Pouring, Wegener, Stein, Barschdorff                           |
| Nitrogen ( $N_2$ )                           | -24                 |                       | -                 | 207        | 3.9                          | -                               | 3     | Arthur   |
| Water ( $H_2O$ )                             | 0 ~ +40             |                       | 6 ~ 15            | -          | 4.4 ~ 5.8                    | -3 ~ 1                          | -     | Barschdorff, Binnie & Green,<br>Gyarmathy & Meyer, Deych et al |

(1)  $T_{mp}$  = melting point temperature.



Table 3 - Experimental Studies of Clusterization in Free-Molecular Jets

| Investigators             | Species  | d (mm)      | P <sub>0</sub> (torr)              | T <sub>0</sub> (K) | Detector     | Results   |
|---------------------------|--|-------------|------------------------------------|--------------------|--------------|---|
| Milne & Greene, 1967      | Ar   | 0.01 ~ 0.1  | (7 ~ 38) · 10 <sup>2</sup>         | 300                | TOFMS        | n <sub>2</sub> (p <sub>0</sub> , d)                                   |
| Golomb et al, 1970        | Ar, NO   | 0.34, 1.17  | 10 ~ 10 <sup>4</sup>               | 300 ~ 1300         | IGD, QMS     | n <sub>2</sub> (p <sub>0</sub> , T <sub>0</sub> )                     |
| Gordon et al, 1971        | K, Rb, Cs  | 0.04 ~ 0.16 | 0.2 ~ 350                          | 300 ~ 900          | VSD          | n <sub>2</sub> (p <sub>0</sub> ), v(p <sub>0</sub> )                  |
| Golomb & Good, 1972       | Ar, Kr, N <sub>2</sub> , O <sub>2</sub> , NO, CO, SO <sub>2</sub> , CO <sub>2</sub>                          | 0.15 ~ 1.25 | ~ 10 <sup>4</sup>                  | 180 ~ 430          | QMS          | n <sub>2</sub> (p <sub>0</sub> , d)                                   |
| Hagena & Obert, 1972      | Ne, Ar, Kr, Xe, N <sub>2</sub> , CO <sub>2</sub>   | 0.15 ~ 1.5  | 10 <sup>2</sup> ~ 10 <sup>4</sup>  | 120 ~ 450          | IGD          | n(p <sub>0</sub> , d)   |
| Dittmers et al, 1972      | Ar, CO <sub>2</sub>  | 0.05        | (7 ~ 45) · 10 <sup>2</sup>         | 300 ~ 600          | TOFMS        | n <sub>2</sub> (p <sub>0</sub> , T <sub>0</sub> ), v(p <sub>0</sub> ) |
| Yealland et al, 1972      | Ar, N <sub>2</sub> , O <sub>2</sub> , CO, CO <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , N <sub>2</sub> O | 0.065, 0.14 | (1 ~ 16) · 10 <sup>2</sup>         | 90 ~ 300           | QMS          | n <sub>2</sub> (p <sub>0</sub> , T <sub>0</sub> )                     |
| Stein & Armstrong, 1973   | H <sub>2</sub> O, CO <sub>2</sub>  | 0.05 ~ 0.28 | (7 ~ 53) · 10 <sup>2</sup>         | 300 ~ 440          | IGD, EBD     | Structure   |
| Sinha et al, 1973         | Ne <sub>2</sub> , K <sub>2</sub>   | 0.12 ~ 0.5  | 50 ~ 300                           | 750 ~ 1055         | Fluorescence | Internal state  |
| Dorfeld & Hudson, 1973    | CO <sub>2</sub>  | 0.07 ~ 0.23 | (4 ~ 9) · 10 <sup>2</sup>          | 300                | MGMS         | n <sub>1</sub> (p <sub>0</sub> )                                      |
| Van Deursen & Reuss, 1973 | H <sub>2</sub>   | 0.028       | 40 ~ 600                           | 26                 | MGMS         | n <sub>1</sub> <sup>+</sup> (p <sub>0</sub> ), v(p <sub>0</sub> )     |
| Good & Golomb, 1974       | Ar, Kr, CO <sub>2</sub> , SO <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO, NO                         | 0.15 ~ 1.25 | 10 <sup>2</sup> ~ 10 <sup>4</sup>  | 85 ~ 430           | QMS, TOFMS   | n <sub>1</sub> (p <sub>0</sub> ), v(p <sub>0</sub> )                  |
| Hagena & Wedel, 1974      | Ar, CO <sub>2</sub> , N <sub>2</sub> — He, Ne  | 0.10        | 10 <sup>2</sup> ~ 10 <sup>4</sup>  | 298                | IGD, TOFMS   | n(p <sub>0</sub> ), v(p <sub>0</sub> )                                |
| Armstrong & Stein, 1974   | H <sub>2</sub> O, CO <sub>2</sub>  | 0.10, 0.28  | (0.7 ~ 53) · 10 <sup>2</sup>       | 300                | IGD, EBD     | n(p <sub>0</sub> , x)   |
| Searcy & Fenn, 1974       | H <sup>+</sup> (H <sub>2</sub> O) <sub>n</sub>   | 0.10, 0.22  | P <sub>eq</sub> ~ 100              | 30                 | QMS          | n <sub>1</sub> (p <sub>0</sub> )                                      |
| Beylich & Robben, 1974    | Ar   | 3.2 ~ 12.7  | 0.7 ~ 200                          | 78 ~ 300           | TOFMS        | n(p <sub>0</sub> )  |
| Calo, 1975                | H <sub>2</sub> O   | 0.03 ~ 0.22 | 10 ~ 10 <sup>3</sup>               | 100 ~ 200          | QMS          | n <sub>2</sub> (p <sub>0</sub> )                                      |
| Beylich, 1976             | N <sub>2</sub>   | 2 ~ 40      | 10 <sup>-2</sup> ~ 10 <sup>2</sup> | 95 ~ 300           | EBD          | n(x), T(x)  |
| Van Deursen & Reuss, 1977 | Ne, H <sub>2</sub> , N <sub>2</sub> , NO, O <sub>2</sub> , Ne-Ar, He-Ne, H <sub>2</sub> -Ar                  | 0.026       | 1 ~ 10 <sup>4</sup>                | 30 ~ 300           | MGMS         | n <sub>1</sub> (p <sub>0</sub> )                                      |

Detector: TOFMS - time-of-flight mass-spectrometer, IGD - ion gauge detector, QMS - quadrupole mass-spectrometer, MGMS - monopole mass-spectrometer, MGMS - magnetic mass-spectrometer, EBD - electron beam diffraction, VSD - velocity selector detector.

Results: n<sub>1</sub>(x<sub>j</sub>) - i-mer concentration (or relative beam intensity) as a function of x<sub>j</sub>,  
n(x<sub>j</sub>) - cluster concentration (or total beam intensity =  $\sum_{i=2}^{\infty} n_i$ ) as a function of x<sub>j</sub>,  
v(x<sub>j</sub>) - velocity distribution as a function of x<sub>j</sub>.

Table 4 - Theoretical Studies of Clusterization in Free-Molecular Jets

| Investigators          | Species                           | Cluster Size <sup>(1)</sup> | Kinetic Model <sup>(2)</sup> |
|------------------------|-----------------------------------|-----------------------------|------------------------------|
| Milne et al, 1970      | Ar                                | D                           | Ter                          |
| Golomb et al, 1970     | Ar, NO                            | D                           | Ter                          |
| Gordon et al, 1971     | K, Rb, Cs                         | D                           | Ter                          |
| Dorfeld & Hudson, 1973 | CO <sub>2</sub>                   | D, C                        | Ter, Bi                      |
| Beylich & Robben, 1974 | Ar                                | C                           | Bi                           |
| Searcy, 1975           | H <sub>2</sub> O + H <sup>+</sup> | C                           | Bi, Ter                      |
| Calo, 1975             | H <sub>2</sub> O                  | D                           | Ter                          |
| Beylich, 1976          | N <sub>2</sub>                    | C                           | Bi                           |
| Knuth, 1977            | Ar, Kr, Ne                        | D                           | Int                          |

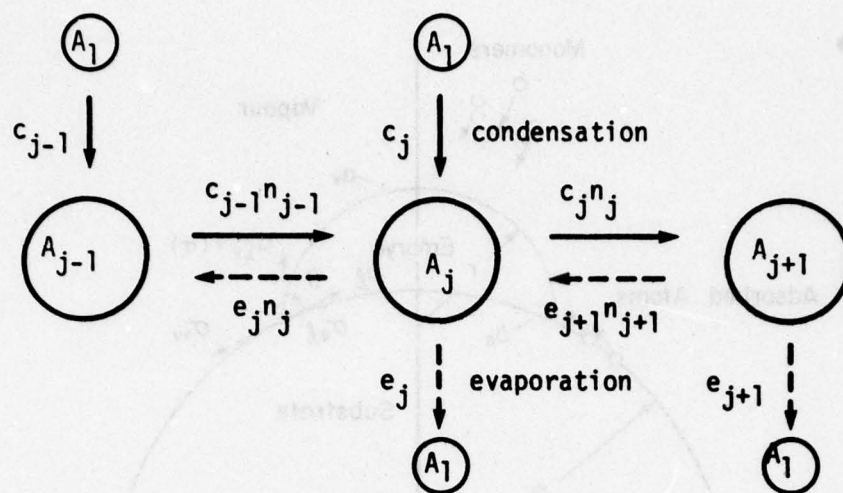
(1) Cluster size: D,  $i = 2$  (dimer); C,  $i \geq 2$

(2) Kinetic model: Ter:  $A_1 + A_1 + A_1 \rightleftharpoons A_2 + A_1$

Int:  $A_1 + A_1 \rightleftharpoons A_2^*$ ,  $A_2^* + A_1 \rightleftharpoons A_2 + A_1$

Bi:  $A_1 + A_1 \rightleftharpoons A_{1+1}$





$$\frac{dn_j}{dt} = c_{j-1}n_{j-1} - e_j n_j - c_j n_j + e_{j+1}n_{j+1}$$

FIG. 1 MULTISTATE KINETICS OF CLUSTERIZATION.

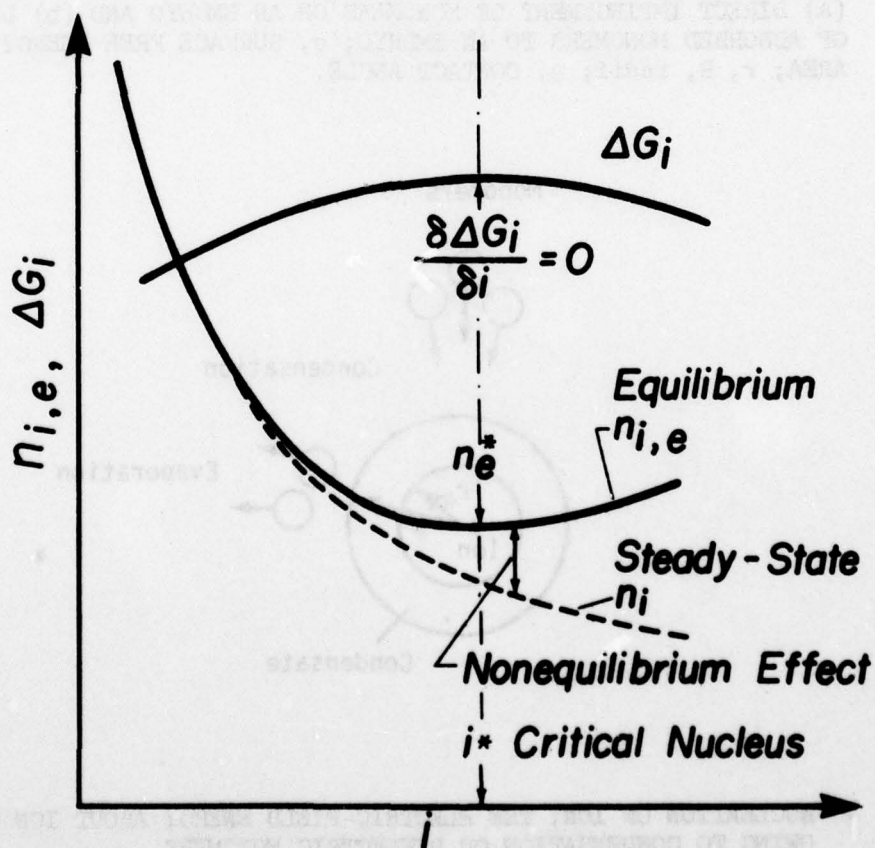


FIG. 2 FREE ENERGY OF CLUSTER FORMATION ( $\Delta G_i$ ) AND EQUILIBRIUM AND STEADY-STATE NUMBER DENSITY OF CLUSTER ( $n_{i,e}$ ,  $n_i$ ) AS A FUNCTION OF CLUSTER SIZE.

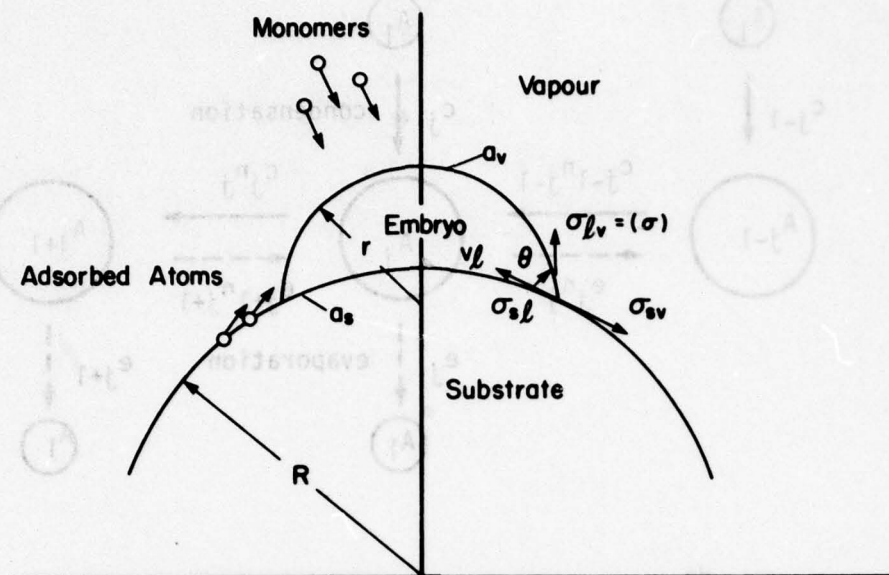


FIG. 3 HETEROGENEOUS NUCLEATION AND CONDENSATION ON A SOLID PARTICLE BY (a) DIRECT IMPINGEMENT OF MONOMERS ON AN EMBRYO AND (b) DESORPTION OF ADSORBED MONOMERS TO AN EMBRYO;  $\sigma$ , SURFACE FREE ENERGY;  $a$ , SURFACE AREA;  $r$ ,  $R$ , radii;  $\theta$ , CONTACT ANGLE.

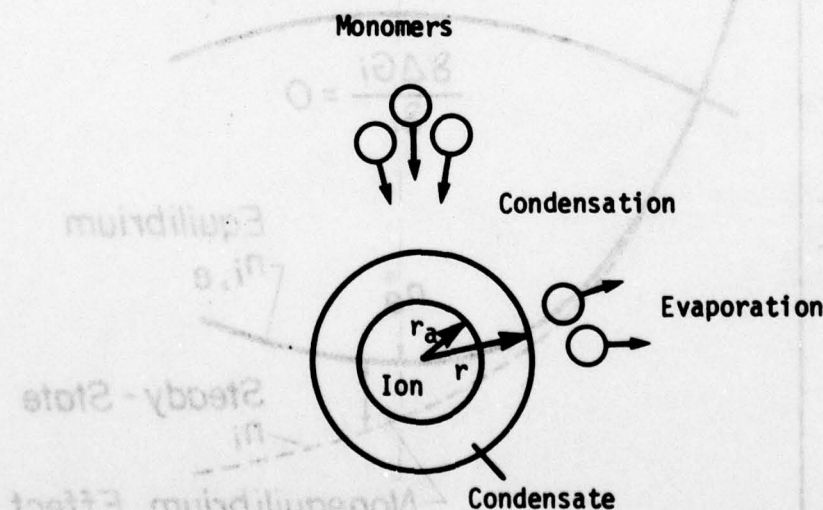


FIG. 4 NUCLEATION ON ION; THE ELECTRIC-FIELD ENERGY ABOUT ION CHANGES OWING TO CONDENSATION OF DIELECTRIC MONOMERS.



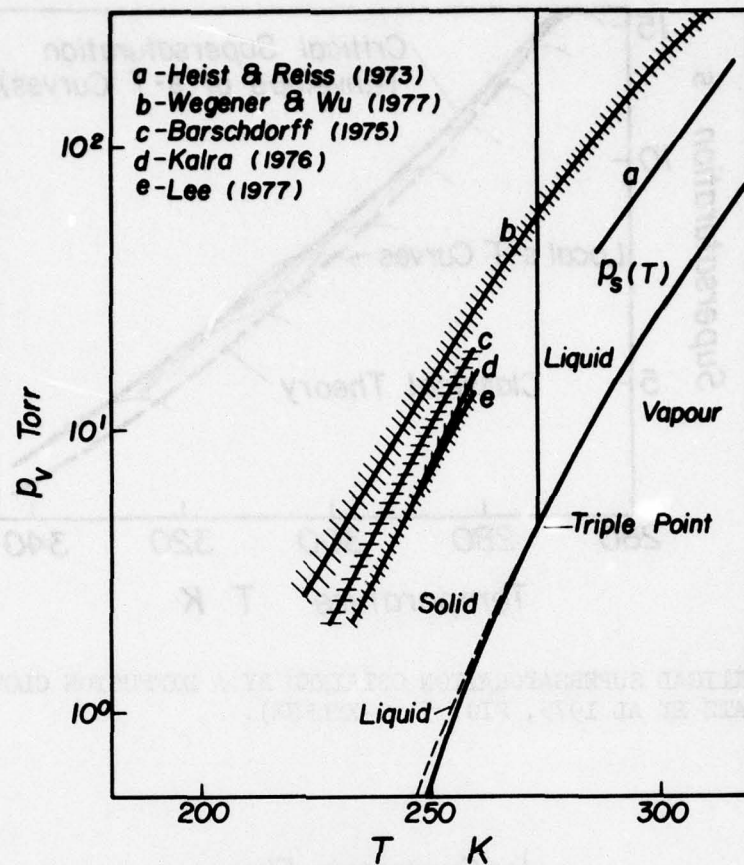


FIG. 5 ONSET CONDITIONS FOR CONDENSATION OF WATER IN VARIOUS FLOWS; DIFFUSION CLOUD CHAMBER (HEIST & REISS), SUPERSONIC-NOZZLE FLOW (WEGENER & WU), SHOCK-TUBE FLOW (BARSCHDORFF, KALRA, LEE).

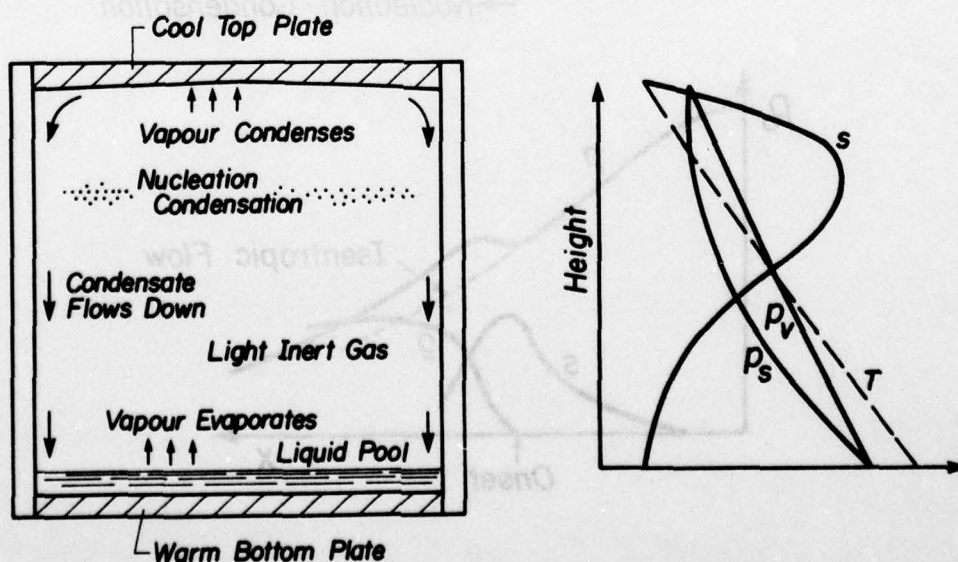


FIG. 6 DIFFUSION CLOUD CHAMBER.

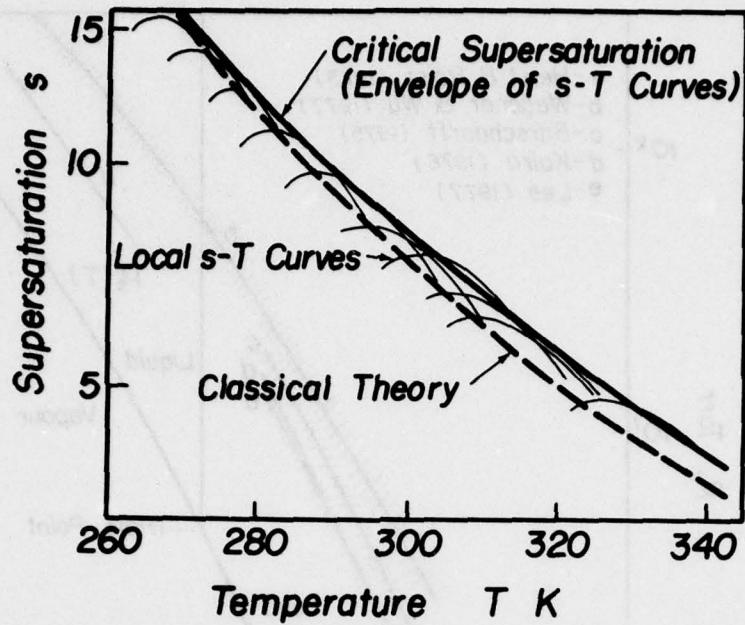


FIG. 7 CRITICAL SUPERSATURATION OBTAINED BY A DIFFUSION CLOUD CHAMBER (KATZ ET AL 1975, FIG. 5; O-XYLENE).

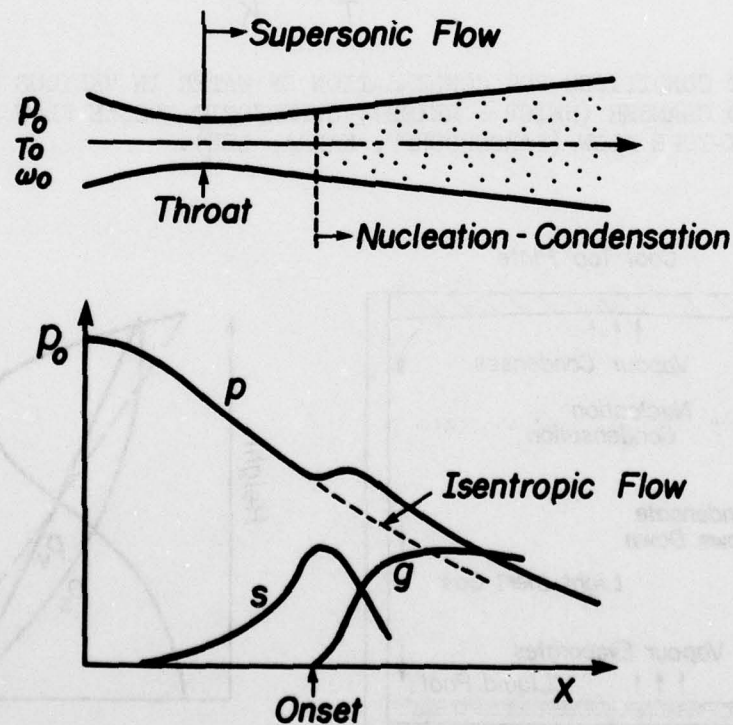


FIG. 8 SUPERSONIC NOZZLE FLOW.



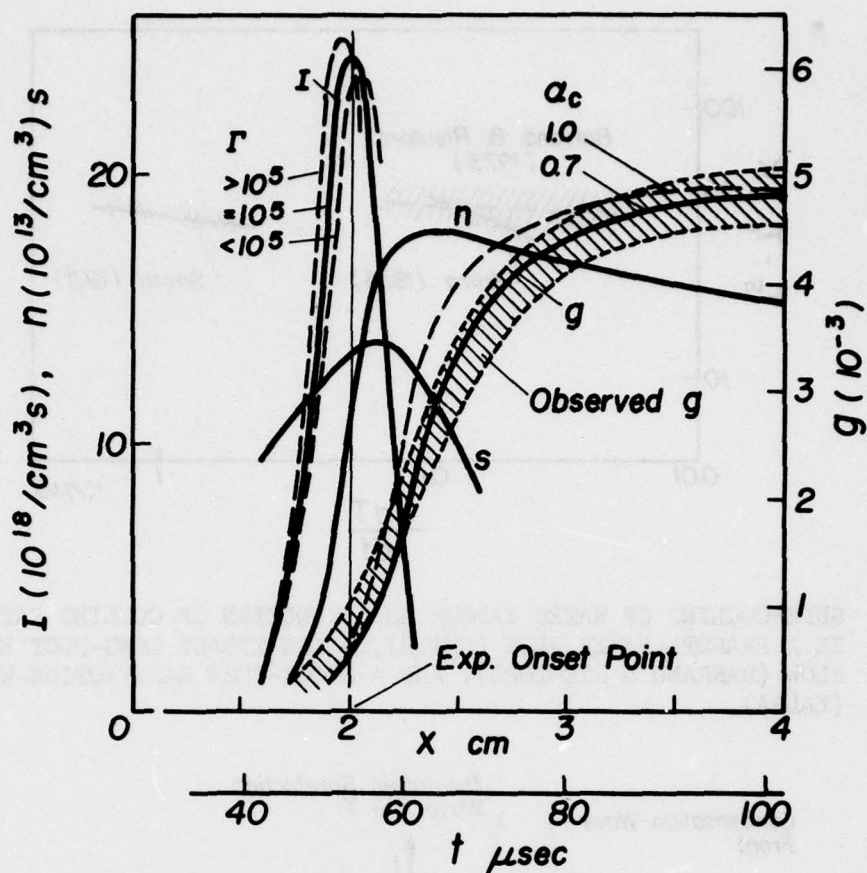


FIG. 9 NUCLEATION AND CONDENSATION IN A SUPERSONIC NOZZLE FLOW (WEGENER ET AL, 1972); ETHANOL-AIR,  $\omega_0 = 0.005$ ,  $\Gamma = 10^5$ ,  $\sigma = \sigma_\infty$ ,  $\alpha = 0.7$ .

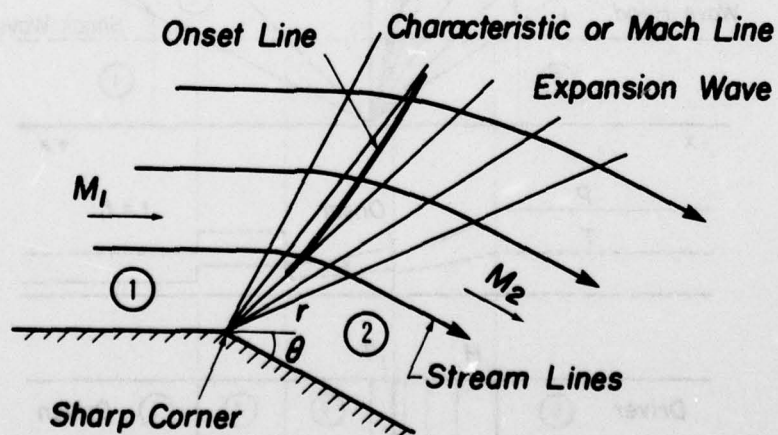


FIG. 10 STEADY PRANDTL-MEYER FLOW.

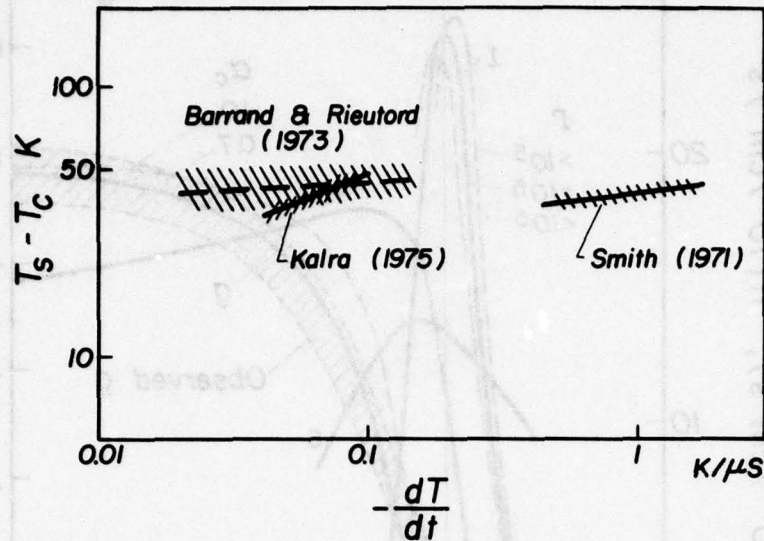


FIG. 11 SUPERCOOLING OF WATER VAPOUR AS A FUNCTION OF COOLING RATE OBSERVED IN A PRANDTL-MAYER FLOW (SMITH), A NON-STEADY LONG-DUCT EXPANSION FLOW (BARRAND & RIEUTORD), AND A SHOCK-TUBE RAREFACTION-WAVE FLOW (KALRA).

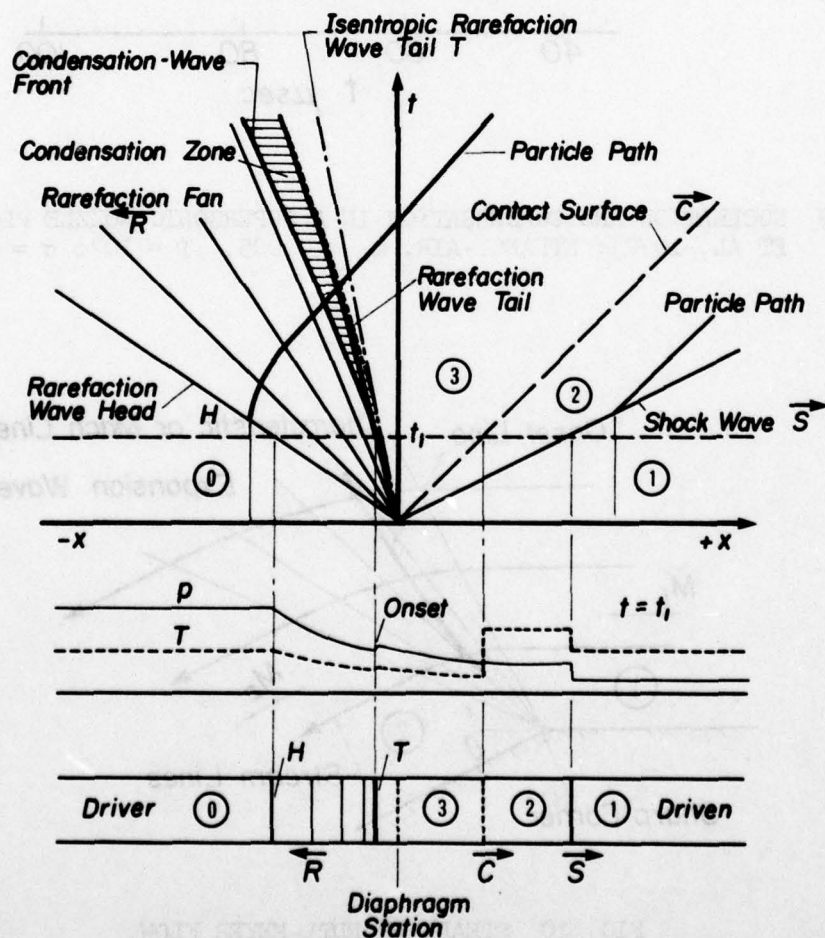


FIG. 12 WAVE SYSTEM PRODUCED IN A SHOCK TUBE. THE SKETCHES SHOW THE PRESSURE AND TEMPERATURE PROFILES, AND THE WAVE POSITION IN THE TUBE AT TIME  $t = t_1$ .



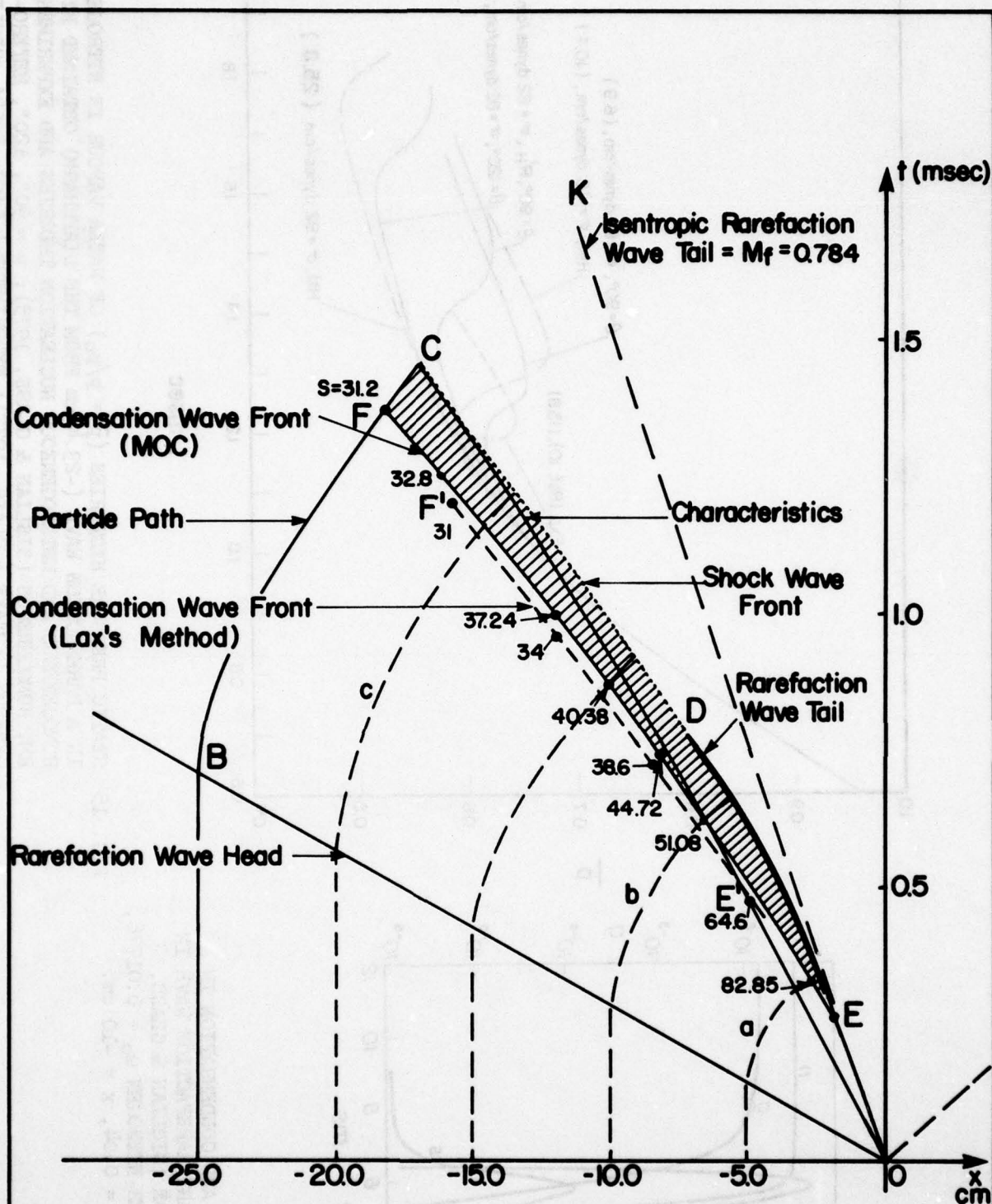


FIG. 13 CONDENSATION-WAVE STRUCTURE IN A NONSTATIONARY RAREFACTION WAVE IN A SHOCK TUBE (SISLIAN & GLASS, 1976); WATER-NITROGEN  $\omega_0 = 0.01776$ ,  $\sigma = \sigma_\infty$ ,  $\alpha_c = 0.04$ .

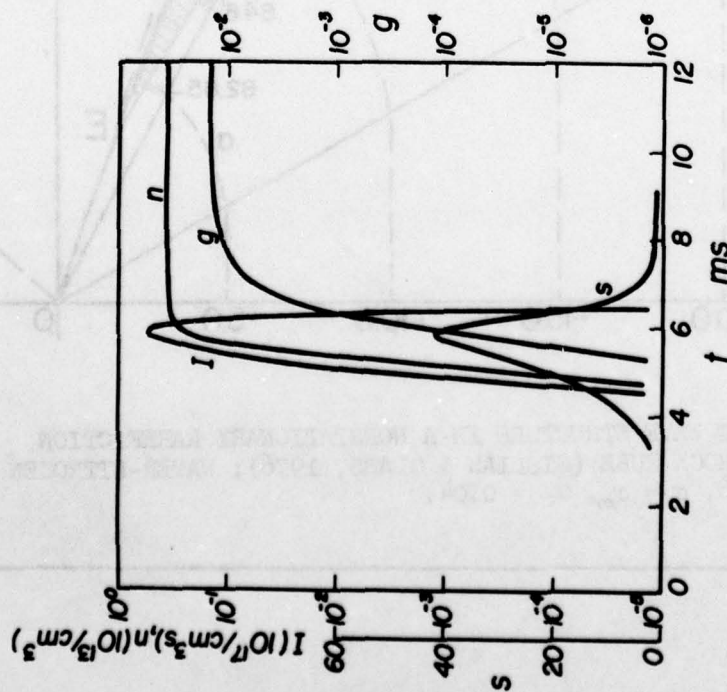


FIG. 14 NUCLEATION AND CONDENSATION IN A NONSTATIONARY RAREFACTION WAVE IN A SHOCK TUBE (SISLIAN & GLASS, 1976); WATER-NITROGEN  $\omega_0 = 0.01776$ ,  $\sigma = \sigma_\infty$ ,  $\alpha_c = 0.04$ ,  $x = -1.0$  cm.

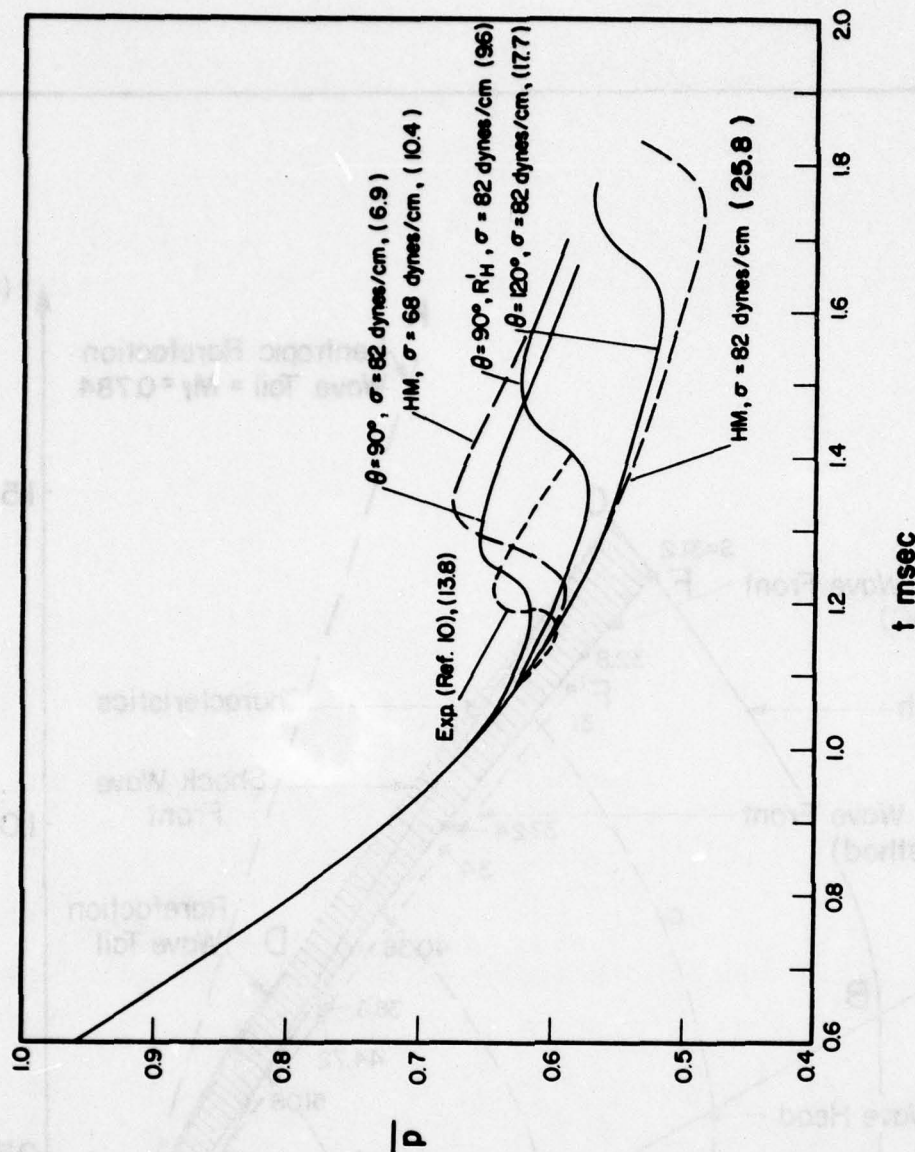


FIG. 15 STATIC PRESSURE HISTORIES ( $\bar{p} = p/p_0$ ) OF WATER VAPOUR IN NITROGEN IN A RAREFACTION WAVE ( $-23.4$  cm FROM THE DIAPHRAGM) OBTAINED BY HOMOGENEOUS AND HETEROGENEOUS NUCLEATION THEORIES AND EXPERIMENT. HM, HOMOGENEOUS (SISLIAN & GLASS, 1975);  $\theta = 90^\circ$ ,  $120^\circ$ , HETEROGENEOUS (KOTAKE & GLASS, 1977); EXPERIMENT (GLASS, KAIRA, SISLIAN & GLASS, 1977); VALUES IN ( ) SUPERSATURATION AT THE ONSET.



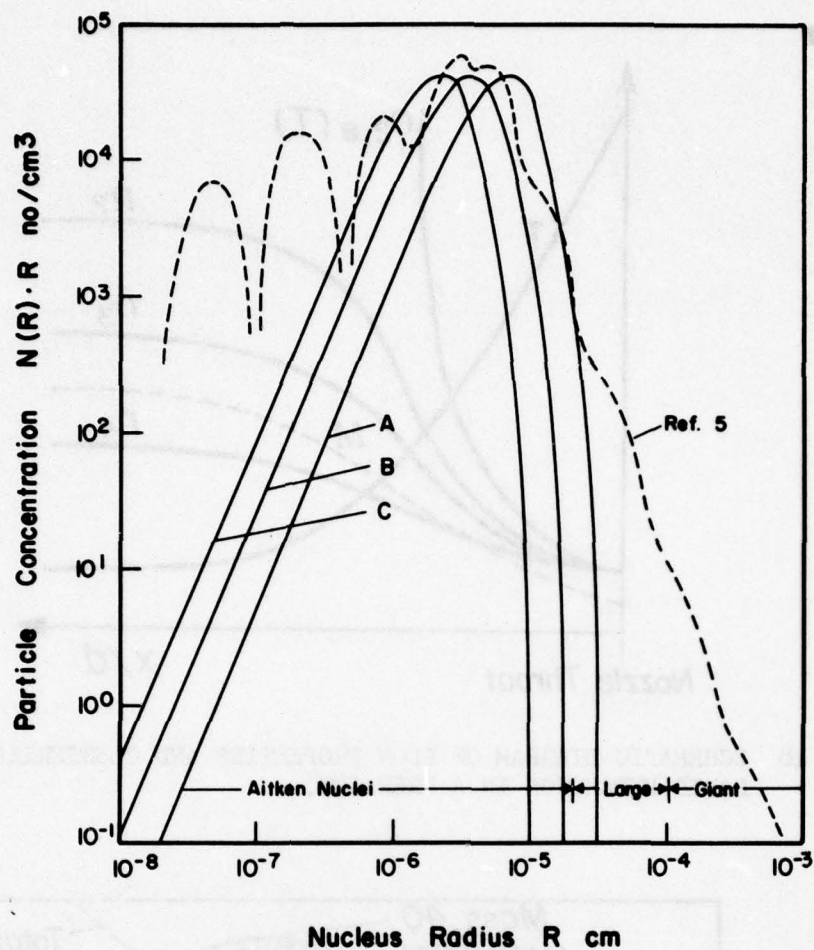


FIG. 16 SIZE DISTRIBUTION OF HETEROGENEOUS AITKEN NUCLEI; THE DOTTED CURVE IS TYPICAL OF ATMOSPHERIC AIR AND APPROXIMATED BY THE SOLID CURVES.

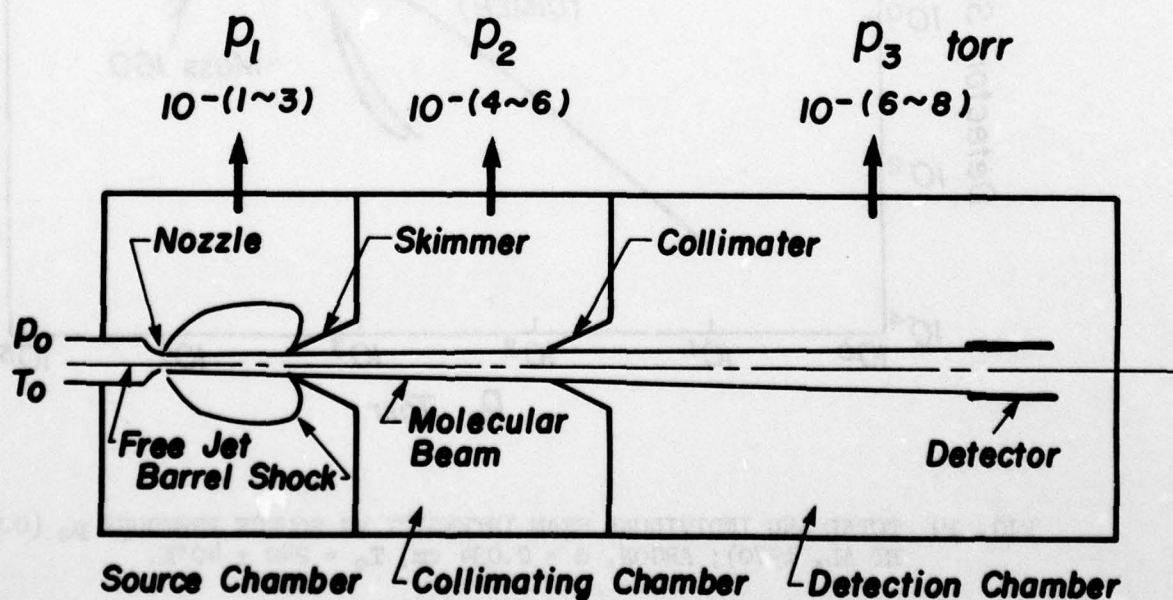


FIG. 17 FREE-MOLECULAR JET.

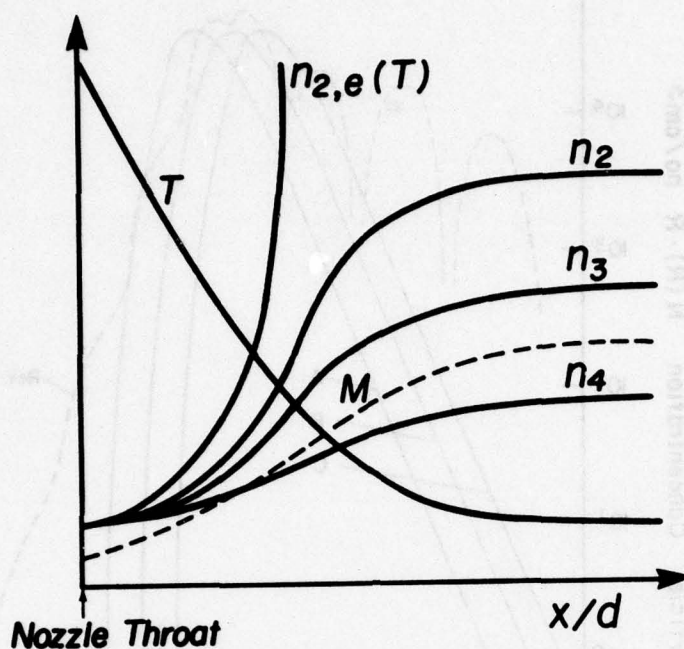


FIG. 18 SCHEMATIC DIAGRAM OF FLOW PROPERTIES AND CLUSTERIZATION THROUGH RAPID EXPANSION IN A FREE JET.

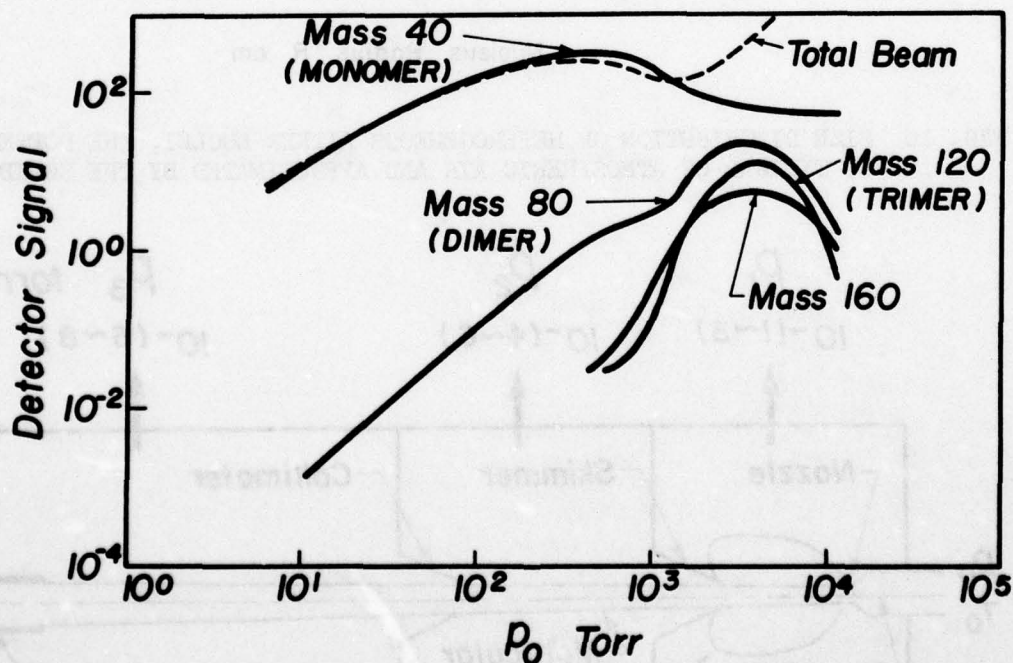


FIG. 19 TOTAL AND INDIVIDUAL BEAM INTENSITY VS SOURCE PRESSURE  $p_0$  (GOLOMB ET AL, 1970); ARGON,  $d = 0.034$  cm,  $T_0 = 240 \pm 40^\circ\text{K}$ .





UTIAS REVIEW NO. 42

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SURVEY OF FLOWS WITH NUCLEATION AND CONDENSATION

Kotake, S. and Glass, I. I. Approx. 80 pages 19 figures 4 tables  
1. Nucleation 2. Condensation 3. Flows with nucleation and condensation

I. Kotake, S., Glass, I. I. II. UTIAS Review No. 42

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